

EXHIBIT D

Green-Duwamish River Watershed

PCB Congener Study: Phase 2 Source Evaluation

Prepared for



Toxics Cleanup Program
Northwest Regional Office
Washington State Department of Ecology
Bellevue, Washington

Prepared by

Dr. Lisa A. Rodenburg

and



Leidos
18912 North Creek Parkway, Suite 101
Bothell, Washington 98011

June 2017

Deposition
Exhibit # 13
Name Rodenburg

Limitation of Use: Leidos' project activities were restricted to analysis of records made available by the Washington State Department of Ecology (Ecology) or third parties during the project. In preparing this report, Leidos has relied on verbal and written information provided by secondary sources and interviews, including information provided by the customer. Leidos has made no independent investigations concerning the accuracy or completeness of the information relied upon. Because the project activities consisted of evaluating a limited supply of information, Leidos may not have identified all potential items of concern and, therefore, Leidos warrants only that the project activities under this contract have been performed within the parameters and scope communicated by Ecology and reflected in the contract. Maps presented in this report were accurate based on the information available to Leidos.

Executive Summary

This report describes the methodology and results of a source evaluation for polychlorinated biphenyl (PCB) congeners in air, sediment, surface water, fish and shellfish tissue, stormwater, and storm drain solids collected in the Green-Duwamish River watershed, and it provides conclusions and recommendations for modeling and the broader source control efforts.

Thousands of environmental samples have been collected in the Green-Duwamish River watershed, and particularly in the Lower Duwamish Waterway (LDW), over the past 30 years. Many of these samples have been analyzed for PCBs, primarily as Aroclors; in recent years, some samples have been analyzed for PCB congeners. PCB congener analysis provides lower detection limits and is a useful tool to identify potential sources of PCB contamination.

In 2016, the Washington State Department of Ecology (Ecology) asked Leidos to prepare a concise and readable summary of available information on PCB congeners and Aroclors that identifies important issues to consider when evaluating historical PCB congener and/or Aroclor data and when collecting new data. As part of the Phase 1 study, Leidos compiled analytical data for PCB congeners in sediment, surface water, fish and shellfish tissue, air deposition, storm drain solids, and stormwater samples from Ecology's Environmental Information Management database and other sources. A total of 36 studies were reviewed, which included over 1,400 samples with data for some or all PCB congeners from over 900 sampling locations within the Green-Duwamish River, LDW, and East and West Waterways.

A second phase of this study was funded by Ecology to identify the types of contaminant sources that are contributing to PCB pollution in the Green-Duwamish River and the LDW using multi-variate statistical techniques ("fingerprinting"). Phase 2 had two primary purposes: provide recommendations about which PCBs to model in the Pollutant Loading Assessment being conducted for the Green-Duwamish watershed, and provide information on potential PCB sources to LDW sediments and surface water.

Positive matrix factorization (PMF) is the statistical technique that was selected for this study. To be usable for PMF, the data must be of sufficient quality, there must be enough data points, most concentrations must be above the detection limit, and information regarding the uncertainty or reproducibility of each data point is needed. Leidos and its subcontractor, Dr. Lisa Rodenburg from Rutgers University, reviewed the data compiled during Phase 1 to better understand the quality of the available data and its usability. An initial data assessment was completed in January 2017; in general, the quality of the data is good. Five environmental compartments (or media) were selected for PMF modeling: air deposition, surface water, sediment, tissue, and storm drains.

The current report details the PMF model and process used to conduct this source evaluation. The analysis was conducted using PMF2 software, and included the following steps:

- Choose analytes (e.g., individual PCB congeners or peaks representing more than one coeluting congener) and samples to be included in the factor analysis.
- Compile input matrices (concentration, detection limits, and uncertainty).
- Run PMF software for numerous factors.

PCB Congener Study Phase 2 - Source Evaluation

- Select the optimal number of factors or fingerprints based on model output.
- Evaluate model results for the selected optimal number of factors.

Results of the PMF modeling tell a coherent story about PCB contamination in the Green-Duwamish watershed for each of the five environmental compartments evaluated. Aroclors are the dominant source of PCBs in the system, with a small contribution from non-Aroclor sources. There are limited data available for some environmental compartments and some locations (particularly surface water in the LDW). Aroclor 1260 is the dominant PCB source type that was observed, followed by Aroclor 1254, Aroclor 1248, and a small contribution from Aroclors 1242/1016. No indication of microbial dechlorination was observed in the data that were available for this evaluation. Results are summarized by environmental compartment below:

- **Air deposition:** 64 samples representing 7 locations within the watershed were used to identify 6 factors (or fingerprints); 4 of the factors resemble the 4 main Aroclors (about 88 percent of the total PCB mass), and 2 factors are not similar to Aroclors but contain non-Aroclor congeners that are frequently associated with pigments (PCB-11 and PCB-209).
- **Sediment:** 53 bed sediment samples and 94 suspended sediment samples were used to identify 5 sediment factors; 3 of these (representing close to 89 percent of the total mass of PCBs) strongly resembled Aroclors.
- **Surface water:** 201 samples were used in the PMF analysis, most collected in the Green River and the East/West Waterways. Very little surface water data were identified in the LDW, and 30 percent of the data points were below the detection limit, severely limiting the usefulness of the data. Because of the data limitations, non-Aroclor congeners were not included in the PMF data set; therefore, the four surface water factors identified all resembled Aroclors.
- **Tissue:** 128 tissue samples collected in the LDW and East Waterway were used to identify 5 factors; these resembled Aroclors 1248 and 1254, as well as weathered Aroclor 1260.
- **Storm drains:** 74 samples of storm drain solids and water, collected from locations throughout the LDW, were used to identify 6 factors; 4 resembled Aroclors, and 2 contained relatively high proportions of non-Aroclor congeners such as PCB-11 and PCBs-206, -208, and -209.

There are many sources of uncertainty associated with the PMF fingerprinting analysis described in this report, including:

- Insufficient data (not enough samples or detected analytes).
- Different models may give different results for the same data sets.
- Various permutations of the same data set may give different model results, even when the same model is used.
- Choosing a sub-optimal number of factors.
- Factors may be misinterpreted.

PCB Congener Study Phase 2 - Source Evaluation

For future source control activities, Aroclor analysis may be useful and sufficient in areas such as storm drains where PCB sources are expected to resemble specific Aroclors and the concentrations are known or expected to be quite high; however, comparing media concentrations to low regulatory values may warrant PCB congener analysis in some situations.

For water quality modeling, additional data are needed to calibrate the models. Modeling of PCBs as homologs is recommended, specifically the tetra- through hepta- homologs, which represent the bulk of the mass of PCBs in the Green-Duwamish watershed. Additional data collection is needed to provide comprehensive spatial coverage for some media, such as surface water, and to provide a sufficient data set for model calibration.

PCB Congener Study Phase 2 - Source Evaluation

Table of Contents

	<u>Page</u>
1.0 Introduction.....	1
2.0 Methodology	3
2.1 Choosing Analytes and Samples.....	3
2.2 Compiling Input Matrices.....	5
2.3 Running Factor Analysis Software	6
2.4 Selecting Optimal Number of Factors	8
2.5 Evaluating Model Results	9
3.0 Results	11
3.1 Air Deposition.....	11
3.1.1 Number of Factors	12
3.1.2 Factor Identification.....	12
3.1.3 Spatial Distribution of Factors	15
3.1.4 Comparison to Other Systems	16
3.2 Sediment	17
3.2.1 Number of Factors	18
3.2.2 Factor Identification.....	18
3.2.3 Spatial Distribution of Factors	20
3.2.4 Comparison to Other Systems	23
3.3 Surface Water.....	23
3.3.1 Number of Factors	24
3.3.2 Factor Identification.....	25
3.3.3 Spatial Distribution of Factors	27
3.3.4 Comparison to Other Systems	27
3.4 Tissue	31
3.4.1 Number of Factors	32
3.4.2 Factor Identification.....	32
3.4.3 Spatial Distribution of Factors	35
3.4.4 Comparison to Other Systems	35
3.4.5 Factor Abundance by Species.....	38
3.5 Storm Drains	38
3.5.1 Number of Factors	40
3.5.2 Factor Identification.....	40
3.5.3 Spatial Distribution of Factors	43
4.0 Modeling Uncertainty.....	47
4.1 Insufficient Data.....	47
4.2 Different Models May Give Different Results When Analyzing the Same Data Set	48
4.3 Various Permutations of the Same Data Set May Give Different Model Results	49
4.4 Choosing a Sub-Optimal Number of Factors	50
4.5 Factors May be Misinterpreted	51
5.0 Conclusions.....	53
5.1 General Observations.....	53
5.1.1 Aroclor Versus Non-Aroclor Sources.....	53

5.1.2	Microbial Dechlorination.....	53
5.1.3	Comparison to Other Systems	54
5.2	Recommendations for Source Control.....	55
5.3	Implications for Water Quality Modeling.....	56
5.3.1	How Much and What Kind of Polychlorinated Biphenyl Data are Available?	56
5.3.2	What is the End Point of Modeling?.....	58
5.3.3	What are the Budget and Time Constraints?	58
5.4	Recommendations.....	58
6.0	References.....	61

Appendices

Appendix A Initial Data Assessment Memorandum
 Appendix B Spatial Distribution Maps

Figures

	<u>Page</u>
Figure 3-1. PCB Congener Fingerprints from Air Deposition Data Set.....	13
Figure 3-2. Relative Abundance of Each of the Six PMF Factors Resolved from the Atmospheric Deposition Data at Each of the Monitoring Sites	16
Figure 3-3. PCB Congener Fingerprints from Sediment Data Set	19
Figure 3-4. Spatial Distribution of PCB Congener Factors in Sediment Samples (Concentrations in $\mu\text{g}/\text{kg}$).....	21
Figure 3-5. Spatial Distribution of PCB Congener Factors in Sediment Samples (Percentage of Total PCBs).....	22
Figure 3-6. PCB Congener Fingerprints from Surface Water Data Set	25
Figure 3-7. Spatial Distribution of PCB Congener Factors in Surface Water Samples (Concentrations in pg/L)	27
Figure 3-8. Spatial Distribution of PCB Congener Factors in Surface Water Samples (Percentage of Total PCBs)	29
Figure 3-9. Mass-Weighted Average Contributions of Each Factor to the Sum of Modeled PCBs for the Surface Water Data Set by RM	30
Figure 3-10. Mass-Weighted Average Contributions of the Four Factors Isolated from the Surface Water Data Set with the Inclusion of PCB-11 (yellow) and PCBs-206+208+209 (black)	30
Figure 3-11. PCB Congener Fingerprints from Tissue Data Set	33
Figure 3-12. Spatial Distribution of PCB Congener Factors in Tissue Samples (Concentrations in $\mu\text{g}/\text{kg}$)	36
Figure 3-13. Spatial Distribution of PCB Congener Factors in Tissue Samples (Percentage of Total PCBs).....	37

PCB Congener Study Phase 2 - Source Evaluation

Figure 3-14. Abundance of Tissue PMF Factors by Species.....	38
Figure 3-15. PCB Congener Fingerprints from Storm Drain Data Set.....	41
Figure 3-16. Spatial Distribution of PCB Congener Factors in Storm Drain Samples (Concentrations in µg/kg and µg/L)	44
Figure 3-17. Spatial Distribution of PCB Congener Factors in Storm Drain Samples (Percentage of Total PCBs)	45
Figure 5-1. PCB Source Types Across Four Watersheds: the New York/New Jersey Harbor (NY/NJ), the Delaware River (DE), the Portland Harbor Superfund Site (PHSS), and the Green-Duwamish Watershed (G-D)	54

Acronyms and Abbreviations

ADME	absorption, distribution, metabolism, and excretion
BDL	below detection limit
CSO	combined sewer overflow
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
GC	gas chromatograph
LDW	Lower Duwamish Waterway
LOD	limit of detection
ng/m ² /day	nanograms per square meter per day
PCA	principle components analysis
PCB	polychlorinated biphenyl
PLA	Pollutant Loading Assessment
pg/L	picograms per liter
PMF	positive matrix factorization
QA	quality assurance
RM	River Mile
RPD	relative percent difference
RSD _G	relative standard deviations of the 'G' matrix across multiple seed runs
RSD _{SR}	relative standard deviation of the surrogate recoveries

1.0 Introduction

The Washington State Department of Ecology (Ecology) and U.S. Environmental Protection Agency (EPA) are jointly developing a Pollutant Loading Assessment (PLA) for the Green-Duwamish River watershed to understand the relationship of water, sediment, and fish tissue quality to the overall health of the watershed, and to determine ways to reduce ongoing sources of pollution. The PLA includes watershed, receiving water, and food web modeling of selected pollutants, including polychlorinated biphenyls (PCBs).

Including all 209 PCB congeners in the model would be impractical in terms of schedule and cost; therefore, Ecology and EPA are looking for recommendations on which PCB congener(s), suite of PCB congeners, homologs, or Aroclor(s) would be the most appropriate candidates for modeling in the PLA. In addition, both agencies are interested in identifying potential sources of PCBs in the Green-Duwamish watershed to inform source control priorities for the Lower Duwamish Waterway (LDW) Superfund site.

Ecology has, therefore, funded a PCB Congener Study in two phases. Phase 1 provided an introduction to PCBs. During Phase 1, Leidos compiled a database of available PCB congener data in the Green-Duwamish River watershed (Leidos 2016). These data included approximately 1,400 samples analyzed for a subset or full suite of PCB congeners in various media, including sediment, tissue, surface water, storm drain solids, stormwater, and air deposition samples.

The objective of Phase 2 was to conduct PCB source evaluation using multi-variate statistical analysis (“fingerprinting”) for the purpose of recommending one or more PCB congeners, suites of congeners, homologs, or Aroclor(s) to be included in the PLA modeling efforts, and to provide information on potential PCB sources to LDW sediments and surface water. Positive matrix factorization (PMF) was selected as the statistical technique used for this study. An initial data assessment was conducted (Leidos and Rodenburg 2017), which refined the data sets to be used in the PMF model and determined that at least some available data from all five environmental compartments (air, surface water, sediment, storm drains, and biological tissues) were suitable for use (Appendix A).

This report describes the methodology and results of the PMF analysis for PCB congeners in air deposition, sediment, surface water, storm drain, and tissue samples collected in the Green-Duwamish River watershed; describes uncertainties associated with the analysis; and provides conclusions and recommendations for the PLA modeling effort.

PCB Congener Study Phase 2 - Source Evaluation

2.0 Methodology

During Phase 1 of the PCB Congener Study, relevant environmental sampling results for PCB congeners in the Green-Duwamish watershed were compiled and summarized (Leidos 2016). An initial data assessment was subsequently conducted to confirm the usability of the data for source evaluation (Leidos and Rodenburg 2017). Five media, or environmental compartments, were selected: air, sediment, surface water, tissue, and storm drain solids/water.

The analysis was conducted using PMF2 software, and included the following steps:

- Choose analytes (e.g., individual PCB congeners or peaks representing more than one coeluting congener) and samples to be included in the factor analysis.
- Compile input matrices (concentration, limits of detection [LODs], and uncertainty).
- Run factor analysis software for numerous factors.
- Select the optimal number of factors or fingerprints based on model output.
- Evaluate model results for the selected optimal number of factors.

These steps are detailed below.

2.1 Choosing Analytes and Samples

Data from 19 studies were included in PMF analysis; the studies selected for inclusion are listed in Appendix A. These 19 studies represent a total of 648 samples analyzed for the full suite of 209 PCB congeners, collected from 217 locations in the Green-Duwamish watershed.

Congener Groupings for Analysis

One of the first tasks in the factor analysis was to choose the list of congeners (specifically, chromatographic peaks containing one or more PCB congeners) to be included in each PMF analysis. In previous PMF analyses, it was noted that, while EPA Method 1668 includes analysis of all 209 PCB congeners in approximately 160 peaks (when using the SPB-octyl column), only about 90 of these peaks are typically above the detection limit in most samples. Therefore, these 90 peaks were targeted for PMF analysis. For most of the environmental compartments, however, it was not possible to use the full list of 90 peaks for 3 reasons:

- The use of more than one gas chromatograph (GC) column occasionally meant that peaks had to be summed to produce the same coelution pattern across two columns. In the Green-Duwamish watershed data sets, three different GC columns were used: SPB-octyl, DB-5, and SGE-HT8. These columns measure the 209 PCB congeners in a different number of peaks and with different coelution patterns¹. To combine data measured on two different columns into one data set for PMF analysis, it is necessary to add the concentrations of one or more peaks reported for the first column to equal the concentrations reported for the same congeners in a different set of peaks reported for the other column. This was required for the sediment and storm drain compartments. For

¹ These issues are discussed in more detail in the *Green-Duwamish River Watershed PCB Congener Study: Phase 2, Initial Data Assessment* (Appendix A).

sediment, the SGE-HT8 and SPB-octyl columns were used; combining these data into one set resulted in 80 peaks. For the storm drain compartment, data from the SPB-octyl and DB-5 columns were combined to yield 73 peaks. (Note that the number of storm drain compartment peaks was further limited by the number of samples; see below.)

- The number of peaks was less than 90 for the surface water data set because not enough measurements of some peaks were above detection. To obtain a data set in which the proportion of non-detected data points was not unreasonably high, the number of peaks was limited to 42, resulting in 30 percent of the data points below detection.
- For the air and storm drain sample sets, the number of peaks was less than 90 because there were not enough samples. The common wisdom is that data sets for PMF analysis should have at least an equal number of samples and analytes or, preferably, more samples than analytes (see Section 3.0). For the air compartment, 64 peaks were used because 64 samples were available. For the storm drain compartment, 73 peaks were used because 74 samples were available.

Available Samples by Medium

The number of samples used in the PMF model for each environmental medium (or compartment) is described below, and described in more detail in Section 3.0:

- **Air deposition:** In the air deposition data set, only the SPB-octyl column was used; however, only 64 samples were available. Therefore, the list of peaks also had to be limited to 64 peaks representing 100 congeners. This data set included about 88 percent of the total PCB mass detected in all air deposition samples from the two studies available².
- **Surface water:** The DB-5 column was used for three surface water samples (Study 22). These three samples were excluded from the PMF data sets to avoid the summing-of-peaks problem noted above because the remaining data were collected using the SPB-octyl column. For surface water, some of the 90 peaks had to be excluded from the data set for PMF analysis because these peaks were below detection limit (BDL) in the vast majority of samples. A total of 209 surface water samples were retained to maximize spatial coverage in the Green River. However, this meant limiting the number of peaks to 42, representing 69 congeners, to keep the total number of non-detect values in the data matrix to a reasonable number (in this case, 30 percent). This PMF analysis included approximately 60 percent of the total measured PCB mass in all available surface water samples.
- **Tissue:** For fish and shellfish tissue, the SPB-octyl column was used for all samples, and enough samples were available that 90 peaks representing 135 congeners could be used in the PMF model. This data set included approximately 96 percent of the total measured PCB mass in all available tissue samples.
- **Sediment:** Two sediment samples were measured using the DB-5 column (Study 22), and these were excluded from the PMF data set. The remainder of the sediment data was

² The percent of mass was estimated by comparing the sum of concentrations across all data points included in the PMF analysis to the total concentration in all measured congeners for the same set of samples, including non-detects assigned a value of one-half the detection limit.

PCB Congener Study Phase 2 - Source Evaluation

measured on both the SPB-octyl and SGE-HT8 columns. Thus, data from these two columns were adjusted via the summing of peaks to provide a consistent set of peaks across both columns, which reduced the total number of peaks analyzed via PMF to 80 peaks representing 154 congeners and included approximately 94 percent of the PCB mass detected in all available sediment samples.

- **Storm drains:** Storm drain samples were analyzed using both the SPB-octyl and DB-5 columns. Only 74 samples were available; therefore, these data were grouped into 73 peaks representing 142 congeners for PMF analysis. These congeners included approximately 92 percent of the total PCB mass detected in all available storm drain samples.

2.2 Compiling Input Matrices

The software used for this analysis (PMF2) requires three input data sets: a concentration matrix, an LOD matrix, and an uncertainty matrix. These were constructed as follows:

- **Concentration matrix:** Analyte concentrations were extracted from the PCB congener database compiled by Leidos during Phase 1 of this project and modified during the current Phase 2. All samples were used whenever possible. Duplicate samples were not averaged; instead, both duplicates were included in the PMF input as separate samples. This was done to provide the largest data sets possible and to evaluate the model performance. This practice also provides an independent check of the reproducibility of the PMF model results because contributions of the various fingerprints should be very similar for both of the duplicates. When concentrations were BDL, they were replaced with a random value between 1 and 100 percent of the LOD. The random number was used instead of other estimates, such as one-half the detection limit, because the detection limits were often estimated and, therefore, somewhat inaccurate. In addition, the estimated detection limits were often the same across all samples in a given PMF input matrix, and using one-half the detection limit would, therefore, have introduced a systematic pattern to the input data. Because the PMF program is looking for such patterns, it was judged best to avoid artificially introducing them into the data.
- **LOD matrix:** LODs were provided for some, but not all, studies. (For a complete accounting, see the *PCB Congener Study: Phase 2: Initial Data Assessment* [Appendix A]). When LODs were not available, the lowest detected concentration by homolog across each sample was calculated, and this value was used as the LOD. In some cases, especially for the nona- and deca-PCB homologs, there are a small number of congeners per homolog, and all of them were detected at high concentrations. In those cases, a reasonable LOD was inferred from the nearest homolog or from a similar sample from the same study.
- **Uncertainty matrix:** The uncertainty matrix is difficult to derive and requires the user to exercise judgment. In previous analyses of EPA Method 1668 data, the relative standard deviation of the surrogate³ recoveries (RSD_{SR}) was used as the uncertainty (Du et al. 2008; Rodenburg et al. 2011, 2015a; Praipipat et al. 2013; Rodenburg and Meng 2013).

³ In this source evaluation, the term “surrogate” is also used to refer to labeled compounds/internal standards as specified in Method 1668.

These generally range from approximately 10 to 30 percent. In the present work, surrogate recoveries were not available for most studies, but were available for Study 5 (sediment), Study 20 (stormwater), and Studies 21 and 22 (surface water, sediment, and storm drain solids). RSD_{SR} for Study 5 ranged from 27 to 53 percent, which is above the typical range observed in other studies. RSD_{SR} for the other studies were generally in the 10- to 30-percent typically observed range. Use of these surrogate recoveries as the uncertainty matrix in PMF2 runs of sediment and storm drain samples led to unstable solutions (i.e., they displayed large variations in ‘Q’ values and high relative standard deviations of the ‘G’ matrix across multiple seed runs [RSD_G], which caused uncertainty in the choice of the number of factors [see Section 2.4]). This may be because the uncertainties from one or two studies were being applied to all studies for a given environmental compartment.

Other metrics of reproducibility were explored. All of the studies reviewed provided at least one sample analyzed in duplicate. The relative percent difference (RPD) for each peak in each duplicate was calculated, and the values by peak across all duplicates were averaged for a given environmental compartment. These average RPDs generally ranged from approximately 5 percent to as high as 150 percent. When these values were used in the uncertainty matrix for the PMF2 analysis, the model results were unstable. This instability may have been caused by the large variability in RPD values. Thus, the RPD values were adjusted to reduce their variability and force them into the 10- to 30-percent range that had worked well in previous analyses by using the following formula:

$$\text{Uncertainty} = 10 \text{ percent} + \text{RPD}/4 \quad (1)$$

This approach preserves the relative differences in uncertainty between congeners. These adjusted uncertainty values worked well in that they produced stable model solutions. Therefore, this was adopted as a standard approach for all data sets.

2.3 Running Factor Analysis Software

There are several techniques for source evaluation. PMF is the technique that was selected as the primary analysis tool for this study. PMF is an advanced factor analysis method developed by Paatero and Tapper (1994). All factor analysis techniques, including PMF and principle components analysis (PCA), define the sample matrix as a product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (2)$$

The sample matrix (X) is composed of ‘n’ observed samples and ‘m’ chemical species. ‘F’ is a matrix of chemical profiles of ‘p’ factors or sources. The ‘G’ matrix describes the contribution of each factor to any given sample, while ‘E’ is the matrix of residuals.

In layman’s terms, the PMF program is seeking to describe the input data matrix (i.e., the measured analyte concentrations) as a linear combination of a small number of sources, each with its own distinct fingerprint. The PMF program does this using the “multilinear engine” (Norris et al. 2009), an algorithm for finding the optimal solution that minimizes E, the difference between the model-predicted concentrations and the measured concentrations. It is important to understand that *no information about the expected source fingerprints is fed into the PMF program*. Specifically in

PCB Congener Study Phase 2 - Source Evaluation

the case of PCBs, the PMF program does not have any information that guides it toward finding fingerprints that resemble Aroclors. When the PMF program does find fingerprints that appear to resemble Aroclors, it is a result of the input data varying in Aroclor-like patterns, not a result of any bias on the part of the PMF model or its operator.

The PMF solution (i.e., ‘G’ and ‘F’ matrices) is obtained by minimizing the objective function ‘Q’ through the iterative algorithm:

$$Q = \sum_{i=1}^n \sum_{j=1}^m (e_{ij} / s_{ij})^2 \quad (3)$$

The calculated ‘Q’ is the sum of the squares of the difference (e_{ij}) between the observations (X) and the model (GF), weighted by the measurement uncertainties (s_{ij}). As a result, lower calculated ‘Q’ values are desirable as they indicate a better fit to the input data. There is also a theoretical value of ‘Q’ equal to $m*n - p*(m+n)$, where ‘m’ is the number of samples, ‘n’ is the number of PCB congeners, and ‘p’ is the number of factors requested (Polissar and Hopke 2001).

PMF has two main advantages over simpler techniques such as PCA. First, in PMF, error estimates for individual values are used to weight the data. The inclusion of uncertainties provides a means for including species with missing values and data that are BDL; highly uncertain measurements are downweighted and have less influence on the solution.

Second, a non-negativity constraint is imposed on the PMF solution. As a result, the PMF solution resembles a chemical mass balance model in which the PMF program attempts to account for all of the mass of the analytes in each sample. This represents another major advantage of the PMF model over PCA, which often generates negative source contributions (Larsen and Baker 2003). PCA sometimes identifies negative source contributions in response to extreme or outlier data values, a symptom of the “nonrobustness” of PCA (Larsen and Baker 2003).

PMF was operated in “robust” mode so that outlier values would not skew the factor profiles (Reff et al. 2007; Norris et al. 2009). Larsen and Baker (2003) compared PCA/multiple linear regression analysis, UNMIX20, and PMF for source apportionment of atmospheric polycyclic aromatic hydrocarbons. PMF was able to identify six source factors from the data set versus four for the other models. PMF has proven to be very effective at understanding PCB sources (Du et al. 2008, 2009; Rodenburg et al. 2010; Praipipat et al. 2013).

Software

Several software packages are available for conducting factor analysis on environmental data. Ecology’s scope of work for this project expressed a preference for publicly available software; therefore, EPA’s PMF 5.0 software was proposed (available for free download at:

<<https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses>>). However, observations of EPA’s PMF 5.0 software have revealed that it sometimes cannot converge on a solution even when the older version (PMF2, which is not publicly available) can, and that the EPA PMF software is less accurate than PMF2 (Rodenburg and Meng 2013; Rodenburg et al. 2015a).

Initial model runs were made using PMF 5.0; the program was not able to converge on a solution for two of the data matrices (sediment and surface water). Varying the input matrices, including the uncertainty matrices, did not resolve the problems. In those cases where PMF 5.0 did converge on a solution, it was significantly different from the solution obtained using PMF2 for the same data set.

Based on professional expertise and preliminary results, two experts on PMF 5.0 (Philip Hopke at Clarkson University and Gary Norris at EPA) suggested that it might not be a suitable program for this project and that PMF2 results could be more useful for the following reasons:

- PMF2 always converged on a solution, even when PMF 5.0 did not.
- PMF2 analysis produced factors that resembled the Aroclor formulations, which may reasonably be expected to be the main PCB sources given the history of PCB production in the United States (see Section 2.5), while the PMF 5.0 results did not.
- PMF2 results told a coherent story about PCB sources across all five environmental compartments.

Therefore, all results presented in this report were derived using the PMF2 software. Uncertainties introduced by choosing PMF2 over PMF 5.0 are explored in more detail in Section 3.0.

2.4 Selecting Optimal Number of Factors

All forms of factor analysis require the operator to identify the optimal number of factors, or source fingerprints, that adequately describe the data set (Reff et al. 2007). The model was run for multiple cases, including varying assumptions of 3 to 7 factors, and the model was run 10 times at 10 different arbitrary starting points (i.e., seed values from 1 to 10) for each case. The output was used to identify how many factors provided the optimal model solution. The current analysis used four main criteria to determine the ‘best’ number of factors. These criteria are similar to those proposed by Reff et al. (2007), except that the comparison of the theoretical and calculated ‘Q’ values was not relied upon to indicate the correct number of factors. This approach was rejected because the calculated ‘Q’ depends on the uncertainty matrix (Equation 3). When uncertainties are inaccurate, the theoretical and calculated ‘Q’ values can differ substantially (Polissar and Hopke 2001).

The first and most important criterion is that the factors must be interpretable and useful for source apportionment of contaminants. For PCBs, this means that most of the resolved factors should at least somewhat resemble the original Aroclor formulations produced by Monsanto, because these are the source of the vast majority of all PCBs produced in the United States. When too many factors are requested, the new factors are often derivatives (i.e., slight modifications) of the original factors. This can cause the model to produce two or more factors that resemble a single Aroclor, which should be avoided.

Second, the model solution should be stable. This is determined by running the model from many different starting points (i.e., seed values) for a given number of factors and determining whether all or most of them converge on the same solution. Similar solutions will have essentially the same ‘Q’ value, ‘G’ matrix, and ‘F’ matrix. The relative standard deviation of 10 seed runs of the ‘G’ matrix is used as an indicator of model stability (RSD_G). As noted above, there are many ways to adjust the input matrix to attain a stable solution. The ‘Q’ value is a

PCB Congener Study Phase 2 - Source Evaluation

function of the similarity between the measured and modeled concentrations. All else being equal, a lower ‘Q’ value indicates a better model fit. Thus, the seed run with the lowest ‘Q’ value is used for all interpretations of the model results.

Third, the model solution should adequately describe the data (i.e., there should be reasonably close agreement between the measured and modeled concentrations). This is primarily evaluated by calculating the unadjusted R^2 value between the measured and modeled concentrations by analyte (i.e., PCB peak). In theory, requesting more factors should allow the model to produce a better fit to the measured data. Deterioration of the model fit when additional factors are requested is usually a sign of over-fitting (i.e., too many factors have been requested).

Low molecular weight (mono- and di-) and high molecular weight (nona- and deca-) PCBs are often less well described by PMF models than those of intermediate molecular weight. This can occur because these congeners come from different (i.e., non-Aroclor) sources than most of the other congeners. For example, PCB-206 and PCB-208 (nona-) and PCB-209 (deca-) are not well described because they originate from pigment sources (i.e., titanium dioxide [Gamboa et al. 1999; Du et al. 2008], as well as some organic pigments such as phthalocyanine green [Hu and Hornbuckle 2010]). Lower molecular weight PCBs, including PCB-11 and PCB-12, are also likely to come from pigments (Rodenburg et al. 2009, 2015c; Anezaki and Nakano 2014; Guo et al. 2014). In addition, lower molecular weight congeners are more susceptible to weathering processes, such as volatilization and aerobic degradation, which may cause variations in their concentrations that are not well described by the PMF model.

Fourth, a multiple linear regression of the ‘G’ matrix versus the measured sum of analytes should yield positive and statistically significant coefficients for all factors. This regression represents a check that Equation 2 adequately describes the data (i.e., the regression is performed on ‘X’ versus ‘G,’ with ‘F’ as the regression coefficients [i.e., slopes] and ‘E’ as the intercept). The regression verifies that all of the generated factors give significant coefficients (‘F’). This ensures that each factor makes a positive and significant contribution to the total mass (‘X’).

2.5 Evaluating Model Results

When evaluating model results, the first task is to try to identify the fingerprints. In the case of PCBs, *a priori* knowledge of the fingerprints that should be produced by factor analysis exists because most of them should resemble Aroclors. The Aroclors were produced by Monsanto, the only North American producer of PCBs, supplying about 99 percent of the domestic market (EPA 1976). Although PCBs can also be produced inadvertently during some chemical processes, these sources are thought to be small relative to the amount of Aroclor PCBs produced and used in the United States. For example, Rodenburg et al. (2015c) have estimated that total inadvertent production of PCB-11, which is formed during production of some pigments, amounts to only about 0.011 percent of all United States PCB production of Aroclors. Thus, it is reasonable to expect that most of the factors generated from PMF analysis should resemble the original Aroclors.

To determine whether the fingerprints generated by the PMF analysis resembled any single Aroclor, the factors were compared with the Aroclor fingerprints of Rushneck et al. (2004). To determine whether any of the factors represented mixtures of more than one Aroclor, a multiple

PCB Congener Study Phase 2 - Source Evaluation

linear regression was performed in which a congener pattern was calculated that represented a linear combination of the four main Aroclors:

$$C_f = aC_{1242} + bC_{1248} + cC_{1254} + dC_{1260} \quad (4)$$

where

C = concentration of the resolved factor (f) or individual Aroclor,
a, b, c, and d = partial regression coefficients.

Coefficients were constrained to be positive, and the best fit (using the least-squares approach) combination was calculated using the Solver feature of Excel. R² values for this best-fit congener pattern versus the factor congener pattern were also calculated.

The second task in interpreting the model output is to examine the 'G' matrix (the concentrations of each factor in each sample) for information about spatial and temporal trends in factor concentrations that might provide clues about the location and intensity of sources. This was done via mapping in ArcMap as well as via time series and other plots.

3.0 Results

This section summarizes results of the PMF2 analysis for air deposition, sediment, surface water, storm drain, and tissue data sets. Figures showing the spatial distribution of factors are provided for each environmental compartment. The first map for each compartment presents the factors in terms of absolute concentrations; the second map presents each of the factors as the estimated percent of total PCB mass in each sample.

3.1 Air Deposition

Studies Considered and Number of Samples

Study Code	Number of Samples Available	Column	Number of Samples Used in PMF Analysis	Number of Field Blanks
16	49	SPB-octyl	49	1
39	15	SPB-octyl	15	none
Total Air Deposition Samples	64		64	1

All 64 samples were included in the PMF model.

Geographic Coverage

The 64 samples include 7 sampling locations representing various land uses; multiple samples were collected at each location between August 2011 and November 2013.

Location Code	Location Name	Location Description
1675	BWR_BeaconHill	Urban residential neighborhood (Beacon Hill)
1676	CER_Duwamish	Industrial land use in an urban area (LDW)
1677	KENT_SC	Suburban, commercial area upstream (Green River)
1678	PSCAA-CW_KentStation	Suburban, commercial area upstream (Green River)
1679	PSCAA-DF_Enumclaw	Rural and forestry land use (Mud Mountain)
1680	SPCC-R_SouthPark	Mix of industrial, commercial, and residential land use (LDW)
2001	SSCC_Georgetown	Mix of industrial, commercial, and residential land use (LDW)

Congeners

Because only 64 samples were available, only 64 peaks were modeled. In the *PCB Congener Study: Phase 2, Initial Data Assessment* (Appendix A), it was suggested that PCB-11, PCB-206, PCB-208, and PCB-209 should be excluded from the data matrix because the sources of these congeners are often pigments rather than Aroclors. However, preliminary runs of air data sets without these congeners produced a factor that was not similar to any of the non-Aroclor congeners. Therefore, these four non-Aroclor congeners were included in the data set. Four Aroclor

PCB Congener Study Phase 2 - Source Evaluation

congeners that made up a relatively small proportion of the PCB mass were eliminated to arrive at a total of 64 peaks. Coeluting congeners in the air deposition data set are listed below.

Coeluting Congeners in Air Deposition Data Set			
18+30	50+53	110+115	171+173
20+28	61+70+74+76	128+166	180+193
21+33	83+99	129+138+160+163	183+185
26+29	85+116+117	135+151+154	198+199
40+41+71	86+87+97+108+119+125	147+149	
45+51	90+101+113	153+168	
49+69	93+95+98+100+102	156+157	

Detection Limits

Detection limits provided for all studies were in units of picograms per liter (pg/L). Because the data were presented in units of flux (nanograms per square meter per day [ng/m²-day]), minimum detected fluxes were used in place of LODs.

Uncertainty Matrix:

RPD of duplicates ranged from 8.8 to 61 percent. These were adjusted using Equation 3 so that uncertainties ranged from 12.2 to 25 percent.

Non-Detects

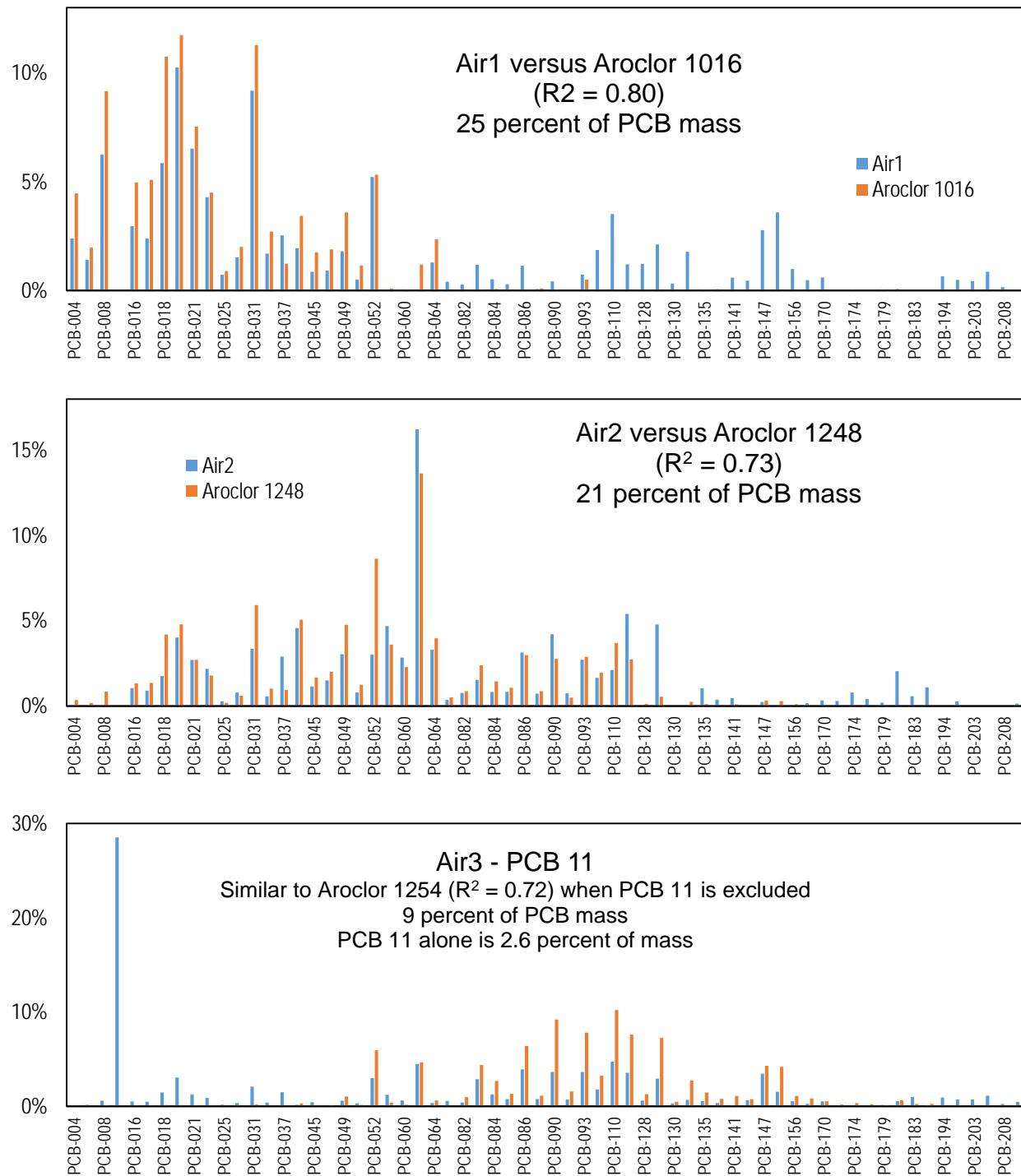
Approximately 18.2 percent of data points were BDL.

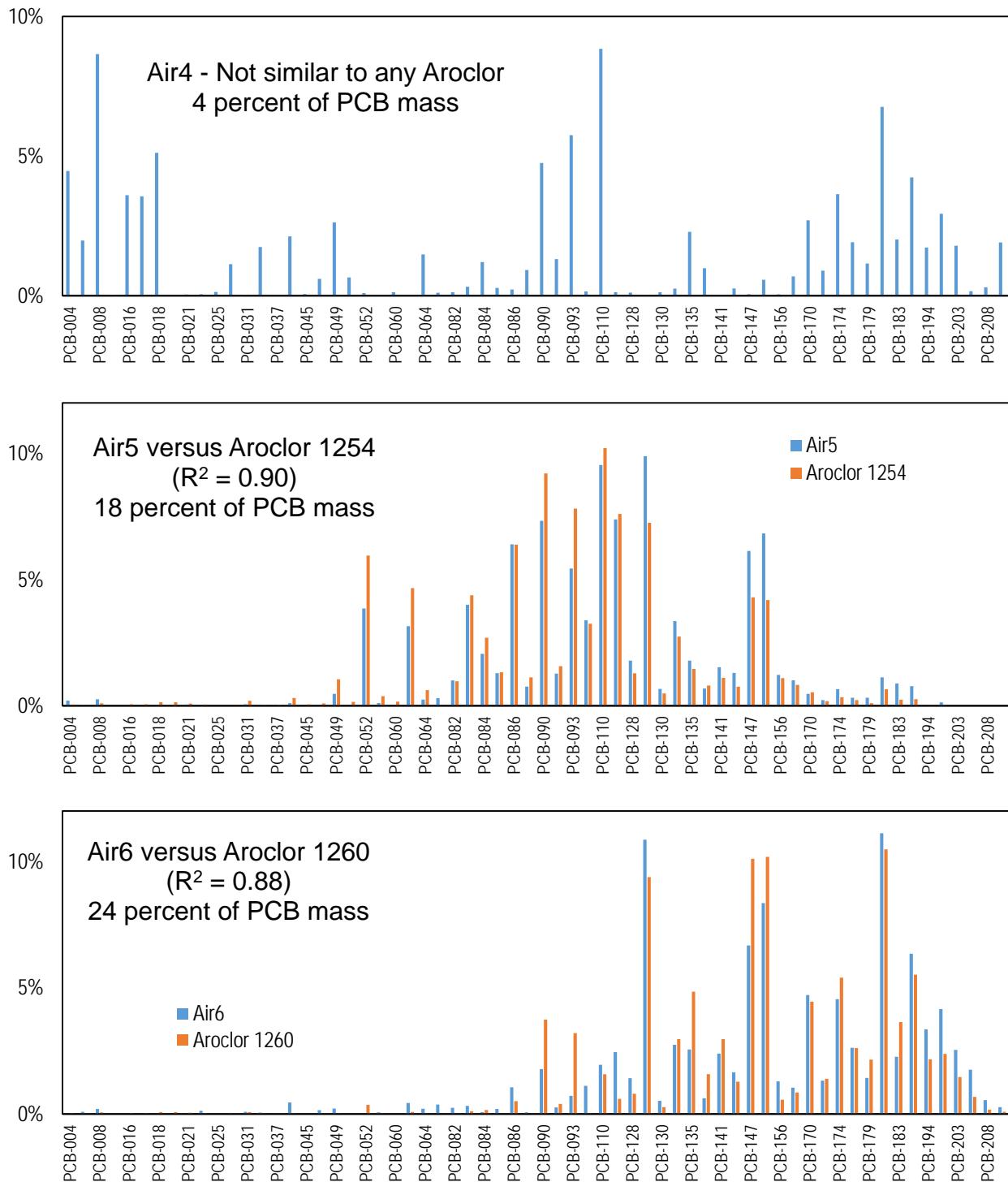
3.1.1 Number of Factors

Six factors were selected based on the criteria outlined above. Six was the largest number of factors that displayed a stable solution (i.e., 9 of the 10 runs of the 6-factor solution agreed with each other, with an average RSD of the G matrix [RSD_G] of just 0.7 percent). The agreement (R^2) between the measured and modeled concentrations was greater than 0.8 for 52 of the 64 peaks. Another eight peaks yielded an R^2 value greater than 0.7. The four congeners with lower R^2 values were PCB-147 ($R^2 = 0.27$), PCB-187 ($R^2 = 0.65$), PCB-195 ($R^2 = 0.55$), and PCB-198 ($R^2 = 0.42$). The six-factor model was interpretable, yielding four factors that resemble the four main Aroclors and two factors that contain high proportions of non-Aroclor congeners.

3.1.2 Factor Identification

The PMF2 solution produces four factors that resemble the four main Aroclors (1242, 1248, 1254, and 1260) and two factors (Air3 and Air4) that are not similar to any Aroclors but contain non-Aroclor congeners such as PCB-11 (Air3) and PCB-209 (Air4) (Figure 3-1). Air3 is dominant in samples 704 and 705 (which are duplicates of each other), comprising 98 percent of sample 704 and 94 percent of sample 705.

*PCB Congener Study Phase 2 - Source Evaluation***Figure 3-1. PCB Congener Fingerprints from Air Deposition Data Set**

*PCB Congener Study Phase 2 - Source Evaluation***Figure 3-1 (Continued). PCB Congener Fingerprints from Air Deposition Data Set****Notes:**

Coeluting groups of congeners are listed under the first congener in each group.
All 64 peaks are shown on graphs, but only 32 are labeled on the x-axis.

PCB Congener Study Phase 2 - Source Evaluation

Factor Air1 likely represents both Aroclors 1242 and 1016, but it better resembles Aroclor 1016 because Aroclor 1016 is a distillation of Aroclor 1242 in which many of the higher molecular weight congeners have been removed (Erickson 1997). This may suggest that Air1 represents low molecular weight Aroclor formulations that have vaporized, because vaporization is similar to distillation. Air1 contains some higher molecular weight congeners than either Aroclor 1016 or 1242. This may represent some mixing of sources during atmospheric transport.

Air5 and Air6 are very similar to Aroclors 1254 and 1260, respectively (R^2 values of 0.90 and 0.88, respectively), which suggests minimal weathering. This suggests that these factors may represent PCBs that have never been in the gas phase because they display minimal mixing or weathering. Instead, they were probably present on dust or soil particles that became airborne and then deposited at the monitoring site. Because particles are scavenged more efficiently out of the atmosphere than gas-phase compounds, contaminants that travel with the particle phase generally do not travel as far as gas-phase contaminants and are, therefore, more likely to be of local origin.

Air3 is dominated by PCB-11 (29 percent of the fingerprint). This factor explains 99.7 percent of all the PCB-11 in the data set. When PCB-11 is excluded from the correlation, the remainder of Air3 resembles Aroclor 1254 ($R^2 = 0.72$), but this is probably not very meaningful because Air3 also contains other congeners that are not present in Aroclor 1254. Notably, although PCB-209 is just 0.5 percent of the fingerprint, Air3 explains 19 percent of the mass of PCB-209 in the data set. Air3 also explains 13 percent of the mass of PCB-206 and 11 percent of the mass of PCB-208. Thus, Air3 explains a significant portion of the mass of all four of these non-Aroclor congeners. Overall, Air3 explains 9 percent of the PCB mass in the data set, but this overstates the importance of non-Aroclor congeners in the atmospheric deposition samples because Air3 includes some Aroclor congeners.

Like Air3, Air4 does not resemble any Aroclor and includes several non-Aroclor congeners. The fingerprint of Air4 includes a 1.9-percent contribution from PCB-209. Air4 explains 37 percent of all the PCB-209 in the data set. This may indicate that Air4 is associated with non-Aroclor PCB sources. Factor analysis of PCB fingerprints in gas-phase air samples collected in Chicago, Illinois (Rodenburg and Meng 2013) and Camden and New Brunswick, New Jersey (Praipipat et al. 2017), similarly yielded factors that were not similar to any Aroclor. At all three locations, these factors were strongly temperature-dependent, and this was interpreted to mean that the factors were associated with secondary PCB sources (i.e., PCBs that were emitted directly to the atmosphere long ago and have re-deposited to surfaces such as soil and then re-volatilized at high temperatures). This process allows many PCB sources to mix, yielding a congener pattern that is not similar to any one Aroclor (Rodenburg and Meng 2013; Praipipat et al. 2017). Because the atmospheric deposition studies analyzed in the present work measured bulk deposition over several days instead of gas-phase concentrations over 24 hours, the temperature dependence of Air4 is difficult to assess.

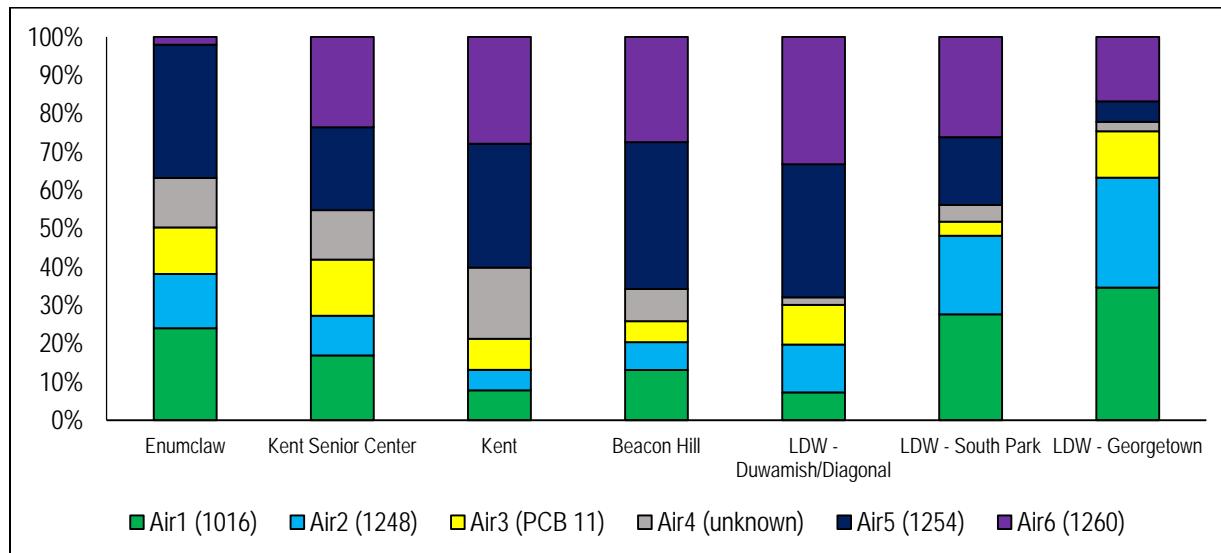
3.1.3 Spatial Distribution of Factors

Maps showing the spatial distribution of the concentrations of the six air deposition factors are shown in Appendix B. In cities such as Philadelphia, Pennsylvania (Du et al. 2009), and Toronto, Canada (Gingrich and Diamond 2001; Harner et al. 2004), lower molecular weight PCB congeners tend to be more abundant in the gas phase at more rural/remote locations. This shift in

the congener/homolog pattern of atmospheric PCBs has been called the ‘urban fractionation effect’ and is thought to occur because lower molecular weight congeners have higher vapor pressures and, therefore, less of their mass is in the particle phase, allowing them to travel farther.

This pattern is observed in the Green-Duwamish air deposition data sets, but only for the sites with lower overall deposition rates (i.e., the five sites to the left in Figure 3-2). The two sites with the highest deposition fluxes (South Park and Georgetown) displayed relatively high fractions of lower molecular weight Aroclors such as 1016, 1242, and 1248. This may indicate that these two sites are impacted by local sources, whereas all other sites are impacted by a more general urban signal.

Figure 3-2. Relative Abundance of Each of the Six PMF Factors Resolved from the Atmospheric Deposition Data at Each of the Monitoring Sites



Note: Sites are ordered by increasing flux from left to right; increasing flux is generally an indicator of increasing urban/industrial character.

3.1.4 Comparison to Other Systems

The fingerprints observed in atmospheric deposition samples from the Green-Duwamish River basin are similar to the gas-phase samples cited above from Chicago, Camden, and New Brunswick in that they are dominated by sources that resemble Aroclors. In the Green-Duwamish River basin, fingerprints strongly similar to Aroclors constitute at least 91 percent of the total PCB mass. PCBs from Aroclors probably constitute more than 91 percent of the total because Air3, which was dominated by PCB-11, also contained some Aroclor-derived congeners, and other Aroclor congeners were excluded from the PCB input matrices. This percentage is similar to Chicago, Camden, and New Brunswick, where at least 75 percent of the gas-phase PCBs were attributable to identifiable Aroclors (Rodenburg and Meng 2013; Praipipat et al. 2017). In these cities, PCBs were measured in the gas phase (not deposition); therefore, the congener patterns would be less likely to resemble Aroclors due to the

PCB Congener Study Phase 2 - Source Evaluation

vaporization process. In addition, these other studies measured PCBs using electron capture detection on a DB-5 column, making the congener patterns more difficult to interpret.

When making comparisons across these studies, it is important to remember that there are significant methodological differences between them. In Chicago, Camden, and New Brunswick, PCBs were measured in the gas phase (not deposition); therefore, the congener patterns would be less likely to resemble Aroclors due to the vaporization process. In addition, these other studies measured PCBs using electron capture detection on a DB-5 column, making the congener patterns more difficult to interpret. Finally, these other studies did not measure PCB-11, PCB-206, PCB-208, or PCB-209; therefore, they would not have been able to identify non-Aroclor sources.

3.2 Sediment

Studies Considered and Number of Samples

Study Code	Number of Samples Available	Column	Number of Samples Used in PMF Analysis	Number of Field Blanks
5	9	SPB-octyl	9	none
6	17	SPB-octyl	17	none
12	14	SPB-octyl	14	2
13	32	SPB-octyl	32	none
22	2	DB-5	0	none
27	7	SPB-octyl	7	none
40	68	SGE-HT8	68	none
Total Sediment Samples	149		147	2

Two samples from Study 22 measured on the DB-5 column were discarded because most of the congeners were BDL (sample codes 2849 and 2388). All other samples were retained, leaving 147 samples.

Geographic Coverage

A total of 53 bed sediment samples were included in the data set:

- 2 samples from 2 locations in the West Waterway,
- 18 samples from 16 locations in the East Waterway,
- 9 samples from 9 locations in the LDW, and
- 24 samples from 6 locations upstream of the LDW (Green River and tributaries).

A total of 94 suspended sediment samples were included in the data set. These were all collected upstream of the LDW: 26 samples at River Mile (RM) 11, and 68 samples from 7 additional locations in the Green River and 4 major tributaries.

PCB Congener Study Phase 2 - Source EvaluationCongeners

After compositing congeners across the SGE-HT8 and SPB-octyl columns, 80 peaks were used in the PMF analysis. Coeluting congeners in the sediment data set are listed below.

Coeluting Congeners in Sediment Data Set			
5+8	50+53	129+138+160+163+ 164	171+173
12+13	61+70+74+76	132+161	180+193
18+30	83+85+86+87+97+99+107+108+ 109+110+111+112+115+116+11 7+119+124+125	134+143	182+187
20+21+28+33	88+91	135+151+154	183+185
26+29	90+101+113	136+148	196+203
40+41+57+64+71+72	93+95+98+100+102	139+140+147+149	197+200
43+44+47+48+49+52+59+ 62+65+69+75	105+127	153+168	198+199
45+51	128+166	1156+157	

Detection Limits

LODs were provided for Studies 5, 12, 27, and 40. For Studies 6 and 13, LODs were estimated from the minimum detected concentrations.

Uncertainty Matrix

RPDs from duplicate samples ranged from 1.8 to 130 percent. These were, therefore, scaled using Equation 3.

Non-Detects

Approximately 8.8 percent of data points were BDL.

3.2.1 Number of Factors

The five-factor solution was selected based on several criteria. Five was the largest number of factors that yielded a low RSD_G of 5.9 percent across all 10 seed runs. For 65 of the 80 peaks, the agreement between the measured and modeled concentrations was R² > 0.9. For another 11 peaks, the R² was greater than 0.6. The following low molecular weight congeners had poor agreement between the measured and modeled concentrations: PCB-1 (R² = 0.13), PCB-3 (R² = 0.24), PCB-11 (R² = 0.45), and PCB-24 (R² = 0.33). Also, the five-factor solution was interpretable.

3.2.2 Factor Identification

Of the five resolved factors, three strongly resemble Aroclors (R² > 0.8) (Figure 3-3). This close similarity between factors Sed2, Sed3, and Sed5 and Aroclors 1248, 1254, and 1260, respectively, suggests very little weathering of the PCB signal. This could indicate that these particular PCB sources are in close proximity to the sediment. Factor Sed1 somewhat resembles Aroclor 1016, although it contains some additional high molecular weight congeners, suggesting

PCB Congener Study Phase 2 - Source Evaluation

extensive weathering and/or mixing. Factor Sed4 does not strongly resemble any Aroclor and contains relatively high amounts of non-Aroclor congeners such as PCB-11 and PCB-209. In the surface waters of the Delaware River and Portland Harbor Superfund site, PCB fingerprints containing a high fraction of PCB-11 were thought to be associated with stormwater and combined sewer overflow (CSO) inputs because this congener was more abundant at high flows (Du et al. 2008; Rodenburg et al. 2015a).

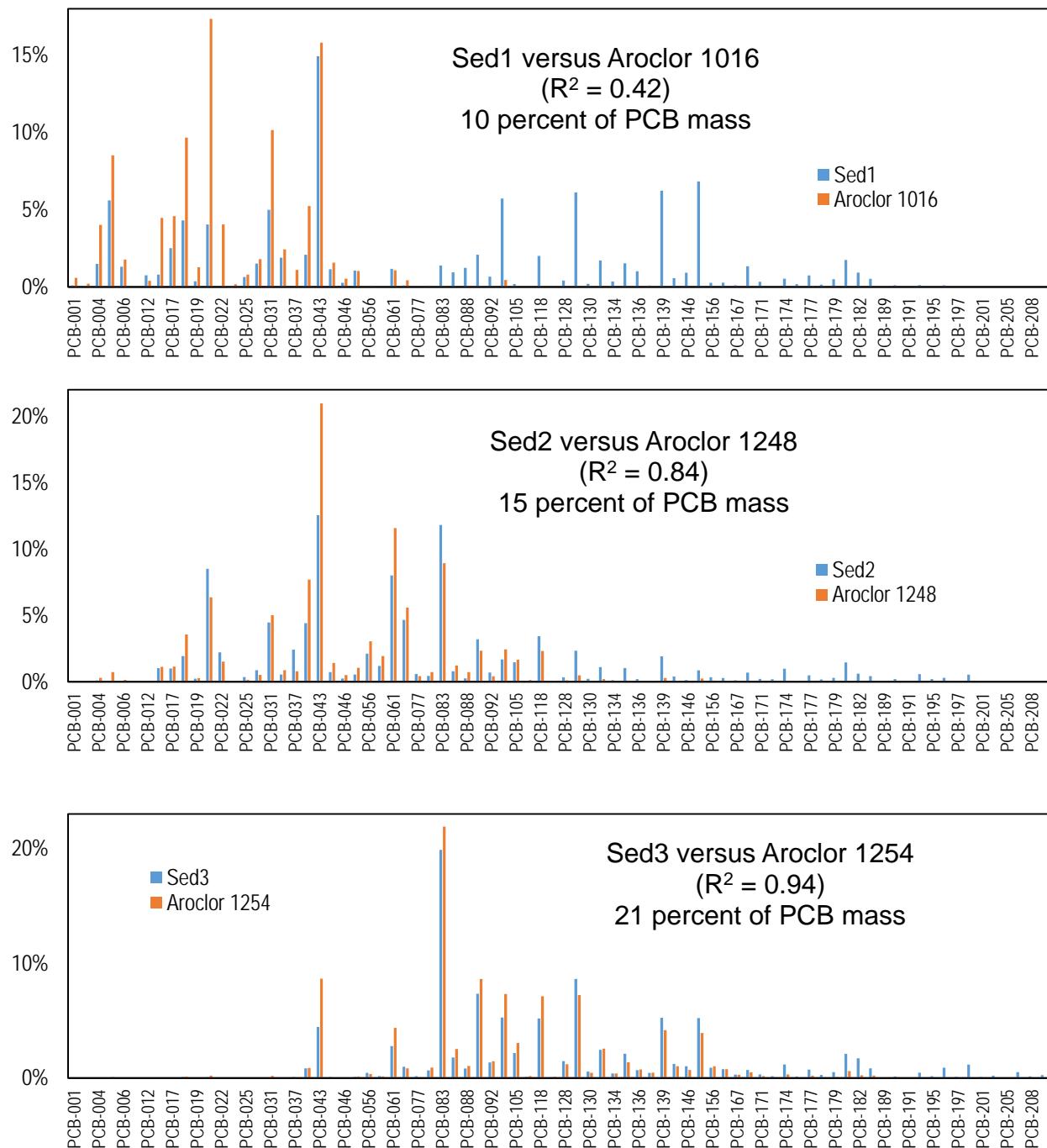
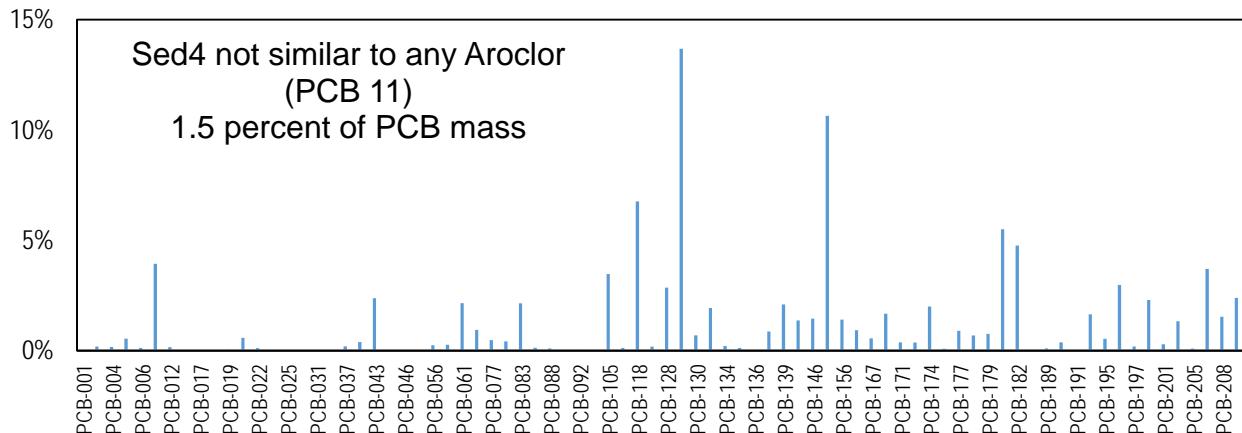
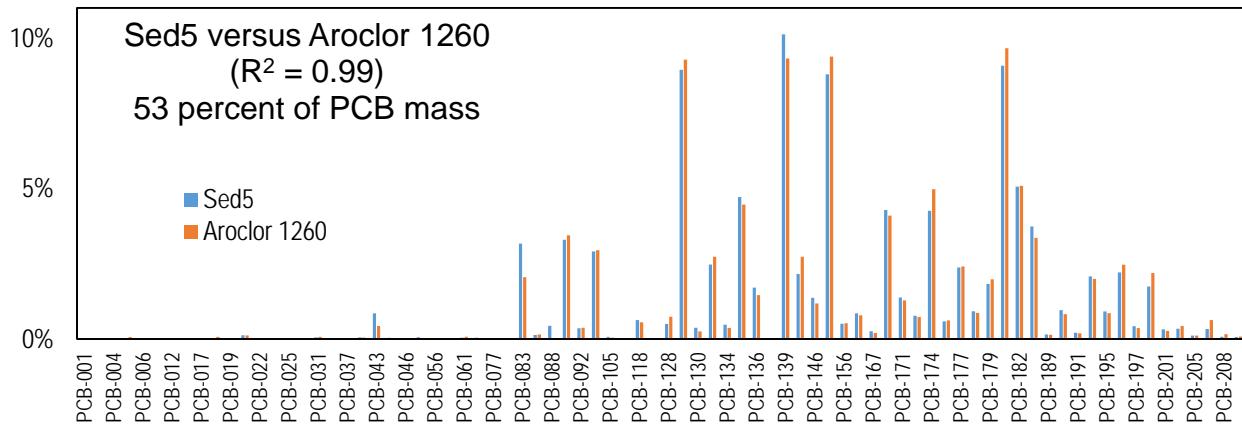
Figure 3-3. PCB Congener Fingerprints from Sediment Data Set

Figure 3-3 (Continued). PCB Congener Fingerprints from Sediment Data Set

Note: Sed4 is not strongly similar to any Aroclor; it contains high proportions of PCB-11 and PCB-209, which are thought to be associated with non-Aroclor sources such as pigments.



Notes:

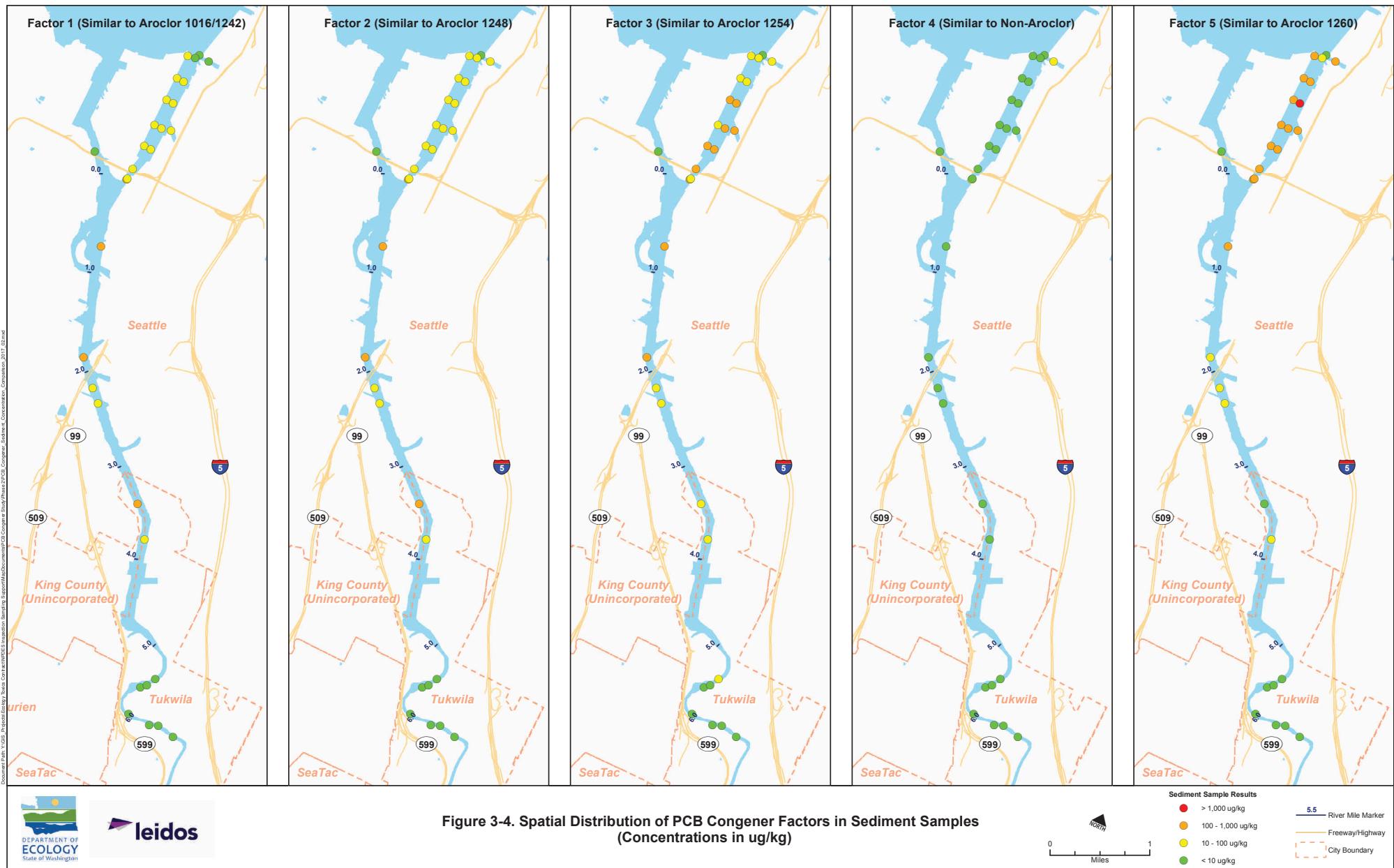
Coeluting groups of congeners are listed under the first congener in each group.

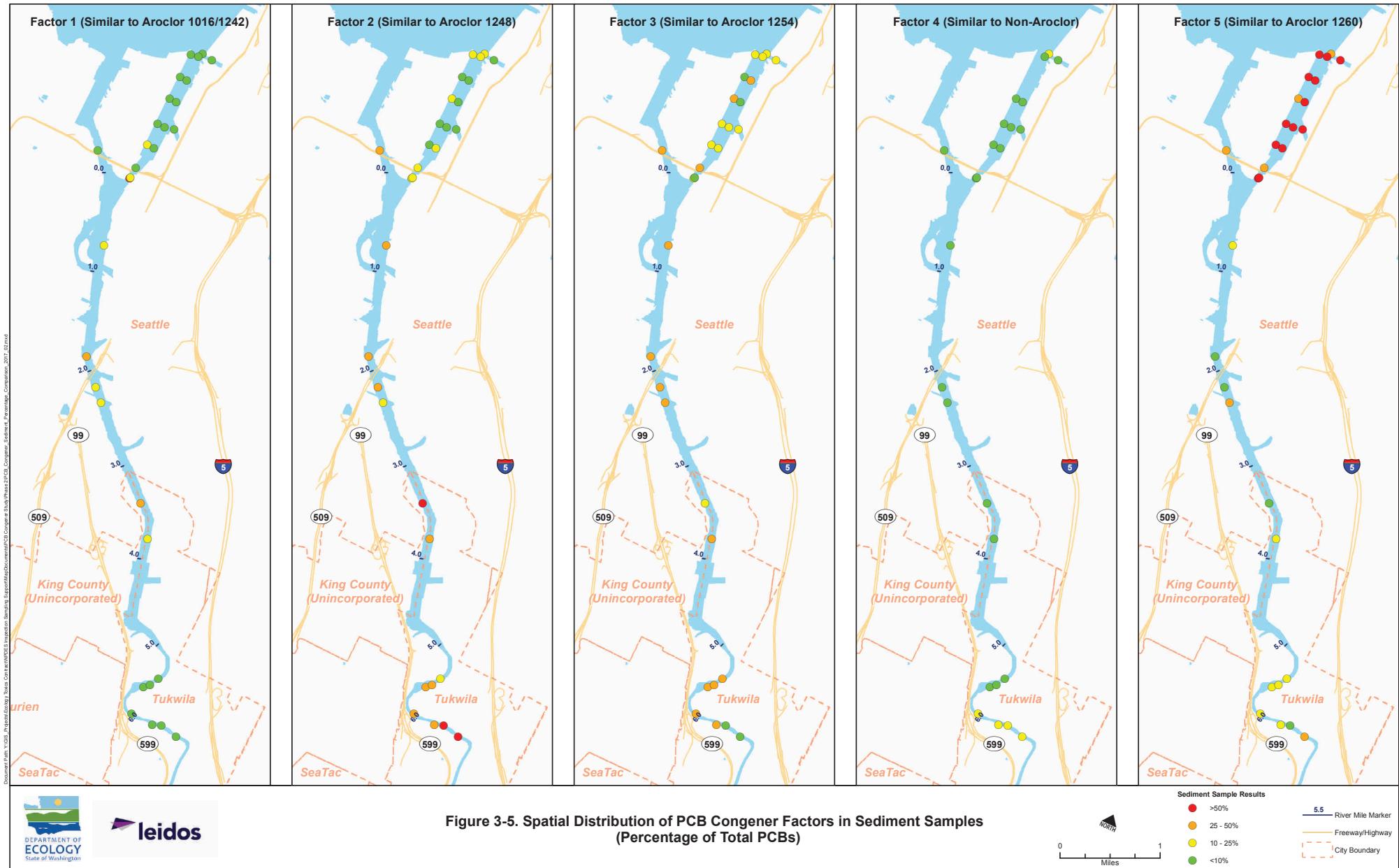
All 80 peaks are shown on graphs, but only 40 are labeled on the x-axis.

Similarly, a factor containing non-Aroclor congeners such as PCB-11 accounted for 1.1 percent of the PCB mass in the sediment of the Portland Harbor Superfund site (Rodenburg et al. 2015a) and was assumed to represent stormwater and CSO inputs there. Because these congeners are present in pigments, and pigments are used in a wide variety of consumer goods, Sed4 may similarly represent a contribution from treated wastewater, stormwater runoff, and CSOs in the Green-Duwamish River study area. It represents just 1.5 percent of the total PCB mass contained in the sediment data set.

3.2.3 Spatial Distribution of Factors

The highest sediment PCB concentrations are observed at the mouth of the LDW east of Harbor Island (Figure 3-4). At this location, the PCB signal is dominated by factor Sed5 (Aroclor 1260) (Figure 3-5). Factor Sed5 also dominates in the Green River around mile point 9.5. The area of high PCB concentration near Allentown is dominated by factors Sed2 and Sed3





PCB Congener Study Phase 2 - Source Evaluation

(Aroclors 1248 and 1254). Further upstream, factors Sed3 (Aroclor 1248), Sed4 (stormwater/wastewater), and Sed5 (Aroclor 1260) dominate. Maps showing the spatial distribution of sediment factors are provided in Figures 3-4 and 3-5, with more detailed maps in Appendix B.

3.2.4 Comparison to Other Systems

A larger fraction of PCBs in the Green-Duwamish River sediment resembles Aroclors than in the New York/New Jersey Harbor and the Delaware River. The Delaware River, in particular, is impacted by non-Aroclor PCBs; PCB-206, PCB-208, and PCB-209 constitute approximately one-half of the PCBs in the sediment due to the manufacture of titanium tetrachloride at a plant in the watershed (Praipipat et al. 2013). In the New York/New Jersey Harbor, about 2 percent of PCBs in the sediment consists of PCB-206, PCB-208, and PCB-209 (Rodenburg and Ralston 2017).

3.3 Surface Water

Studies Considered and Number of Samples

Study Code	Number of Samples Available	Column Used	Number of Samples Used in PMF Analysis	Number of Field Blanks
6	57	SPB-octyl	51	none
12	6	SPB-octyl	6	1
13	21	SPB-octyl	21	10
14	56	SPB-octyl	56	1
15	24	SPB-octyl	24	1
22	3	DB-5	0	none
23	51	SPB-octyl	43	none
Total Surface Water Samples	218		201	13

All of the studies except Study 22 used the SPB-octyl column. Because Study 22 used the DB-5 column and had only three samples, it was excluded from the database. Due to a large number of non-detects, some samples were removed from the surface water data set before PMF analysis.

Geographic Coverage

Of the 201 samples included in the PMF analysis, most were collected in the Green River (upstream of the LDW) and in the East Waterway (downstream of the LDW):

- 51 samples were collected at 6 locations in the East Waterway;
- 9 samples were collected in the West Waterway, just south of the Spokane Street Bridge;
- 10 samples were collected in the LDW at approximately RM 3.3;
- 9 samples were collected just upstream of the LDW at RM 6.5;
- 27 samples were collected upstream of the LDW at RM 11; and

- 95 samples were collected at 11 locations farther upstream of the LDW in the Green River and its tributaries.

At a given location, samples were collected on different dates and at different depths. No attempt was made to separate surface water data by depth collected.

Congeners

To include as many samples as possible, it was necessary to limit the number of peaks to 42 to keep the total number of BDL values below a reasonable value. In limiting the number of peaks this severely, it was decided to exclude PCB-44 and PCB-45 from the data set. These congeners are problematic because they were associated with contamination from silicone rubber encountered in samples from Study 15. Coeluting congeners in the surface water data set are listed below.

Coeluting Congeners in Surface Water Data Set			
18+30	85+116+117	129+138+160+163	183+185
26+29	86+87+97+108+119+125	135+151+154	198+199
40+41+71	90+101+113	147+149	
49+69	110+115	153+168	
50+53	128+166	180+193	

Detection Limits

LODs were given for Studies 6, 12, 13, and 14. LODs from Study 12 were often higher than the detected concentrations; therefore, they were not used. For Studies 12, 15, and 23, the LODs were inferred from the lowest detected concentrations.

Uncertainty Matrix

The uncertainty matrix was based on the RPDs from duplicate samples, which ranged from 5 to 52 percent. These were, therefore, scaled using Equation 3.

Non-Detects

The data matrix consisted of 201 samples and 42 peaks, and 30 percent of the data points were BDL. This high proportion of BDL values suggests that the agreement between the measured concentrations and model predictions was less accurate than for most of the other data sets considered in this report.

3.3.1 Number of Factors

The four-factor solution was selected based on several criteria. Four factors yielded a stable model solution with an RSD_G of 0.3 percent. The four-factor model was also interpretable.

Non-Aroclor congeners, including PCB-11 and PCB-209, were not included in this data set. The high molecular weight congeners (PCB-206, -208, and -209) are not very soluble in water; therefore, it is not surprising that they were below detection in most samples. Despite its greater water solubility, PCB-11 was also below detection in more than half of the samples.

PCB Congener Study Phase 2 - Source Evaluation

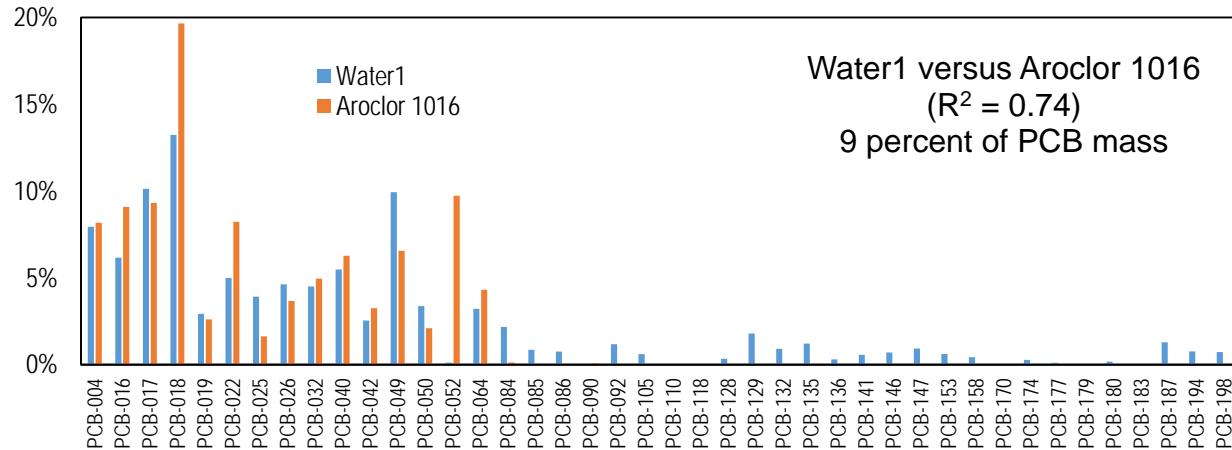
The agreement between the measured and modeled concentrations (R^2) was very good, considering the high proportion of BDL values: greater than 0.8 for 29 of the 42 peaks. Another eight peaks yielded R^2 values between 0.7 and 0.8. Peaks that were not well reproduced by the model were PCB-4 ($R^2 = 0.51$), PCB-19 ($R^2 = 0.28$), PCB-22 ($R^2 = 0.67$), PCB-25 ($R^2 = 0.60$), and PCB-194 ($R^2 = 0.60$). These five congeners had relatively larger proportions of BDL values than the other congeners.

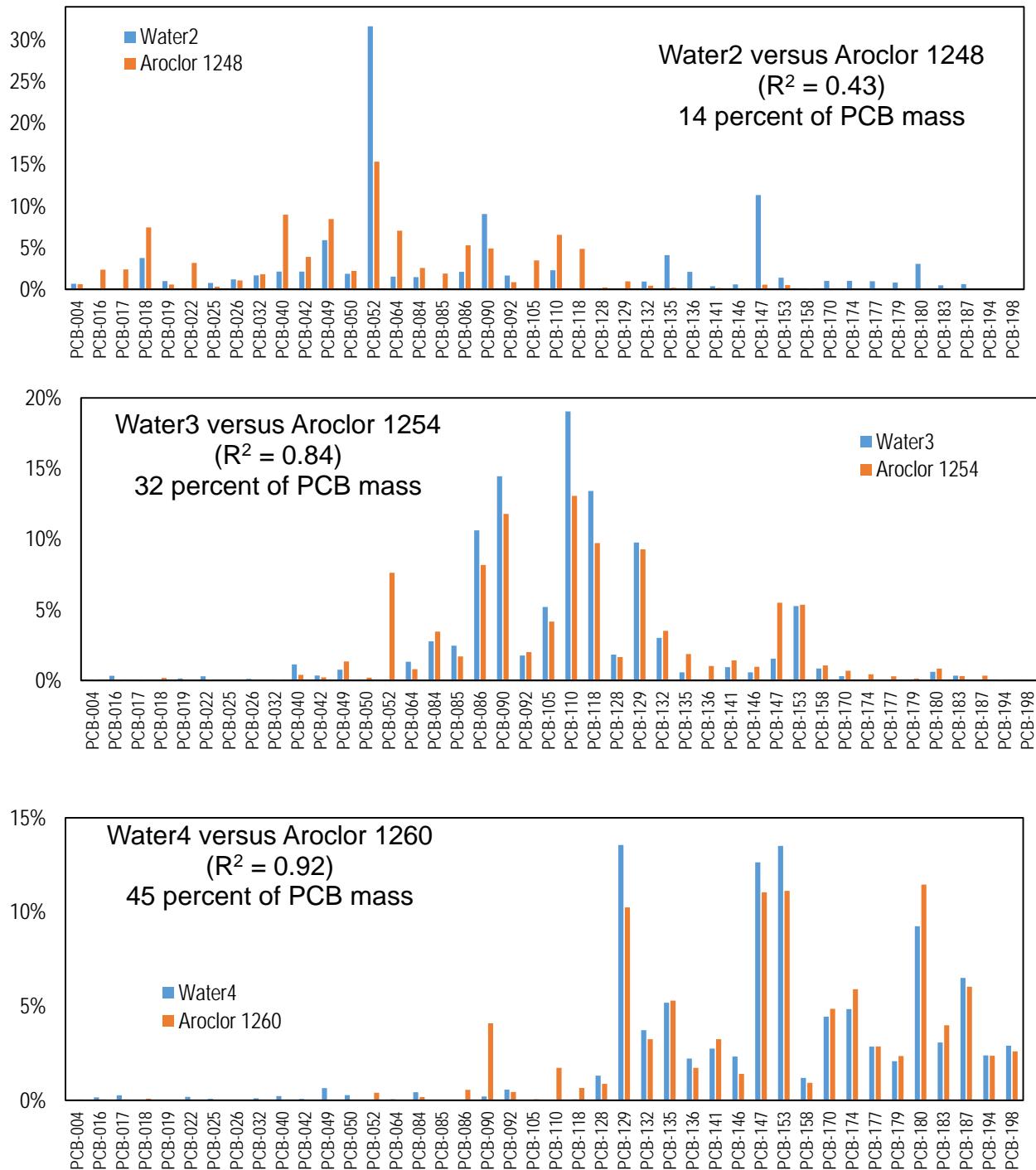
In the *PCB Congener Study: Phase 2, Initial Data Assessment*, it was noted that the congeners most associated with contamination from silicone rubber were (in decreasing order of likelihood) PCB-44+47+65 and PCB-45+51 (which were excluded from the PMF data set), as well as PCB-25, PCB-21+33, and PCB-17. PCB-21+33 and PCB-17 were well predicted by the PMF model, suggesting that contamination due to silicone rubber is not having a large effect on the PMF solution. It is possible that PCB-25 is not well predicted by the model because it is associated with the contamination from silicone rubber in Study 15. However, the worst outlier for this congener was Sample 3057 from Study 6; when this sample was removed from the correlation, the agreement between measured and modeled concentrations of PCB-25 improved to 0.79. Thus, it can be concluded that contamination from silicone rubber (and elimination of PCB-44 and PCB-45 from the data set) did not significantly impact the PMF model solution for surface water.

3.3.2 Factor Identification

All four of the factors at least somewhat resembled Aroclors (Figure 3-6). Water4 was very similar to Aroclor 1260 ($R^2 = 0.91$) and comprised 45 percent of the PCB mass in the data set. Aroclor identification of the other factors is less certain due to the relatively short congener list and high number of BDL values. Water3 is similar to Aroclor 1254 but has less PCB-52 than the Aroclor. Water2 is similar to Aroclor 1248 but has more PCB-52 than the Aroclor. Similarly, Water1 is somewhat similar to Aroclor 1016 but contains less PCB-52 than the Aroclor. It may be that the PMF model had difficulty apportioning the mass of PCB-52 among these three factors. This is the kind of difficulty that PMF encounters with data sets containing numerous BDL values and a short congener list. PCB-52 may be the most difficult congener for the model to predict because it is abundant in all three of these Aroclors.

Figure 3-6. PCB Congener Fingerprints from Surface Water Data Set



*PCB Congener Study Phase 2 - Source Evaluation***Figure 3-6 (Continued). PCB Congener Fingerprints from Surface Water Data Set****Note:**

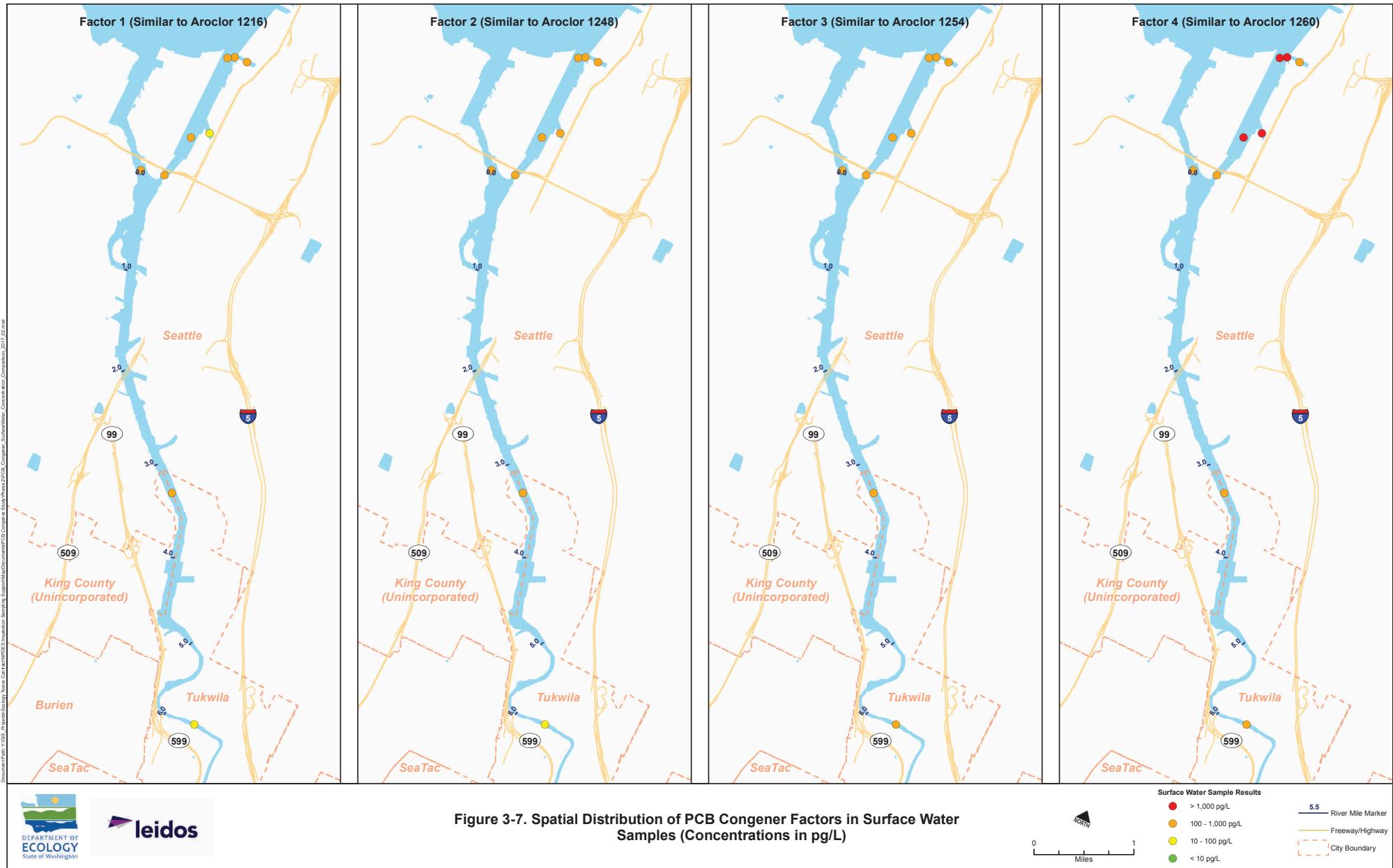
Coeluting groups of congeners are listed under the first congener in each group.

3.3.3 Spatial Distribution of Factors

The spatial distribution of the surface water factors is displayed by concentration in Figure 3-7 and by fraction of total PCBs in Figure 3-8. Water column concentrations of PCBs are lower in the upstream portions of the study area (i.e., in the Green River). Downstream portions are dominated by Water3 (Aroclor 1254) and Water4 (Aroclor 1260), in agreement with the sediment and biota results. The contribution of each factor as a percent of total PCB mass is presented by RM in Figure 3-9. Surface water was the only one of the five compartments for which non-Aroclor PCBs, such as PCB-11, PCB-206, PCB-208, and PCB-209, were not included in the data set analyzed by PMF. Therefore, in Figure 3-10, the same data are presented but with the addition of these congeners to demonstrate their relative importance as PCB sources. Note that the average contribution of PCBs-206+208+209 at RM 33.2 is quite high, but this is due to one sample (681) that contained 208 pg/L of these three congeners. In all other samples from this location, PCB-206, PCB-208, and PCB-209 were BDL. More detailed maps of the spatial distribution of surface water factors are provided in Appendix B.

3.3.4 Comparison to Other Systems

Because these non-Aroclor congeners were not included in the PMF input, it is more difficult to make direct comparisons between the PCB sources in the Green-Duwamish River and those in other river systems. At the Portland Harbor Superfund site, a fingerprint representing dechlorinated PCBs comprised about 22 percent of all the PCBs in surface water (Rodenburg et al. 2015a). In the New York/New Jersey Harbor, a fingerprint resembling dechlorinated Aroclor 1242 represents about 32 percent of PCBs in the surface water and is attributable to inputs from the Upper Hudson River (Rodenburg et al. 2011). The lack of a dechlorination signal in the Green-Duwamish River surface water is not due to the short congener list analyzed because major dechlorination products such as PCB-4 and PCB-19 were included. Dechlorination is discussed in more detail in Section 5.1.2.



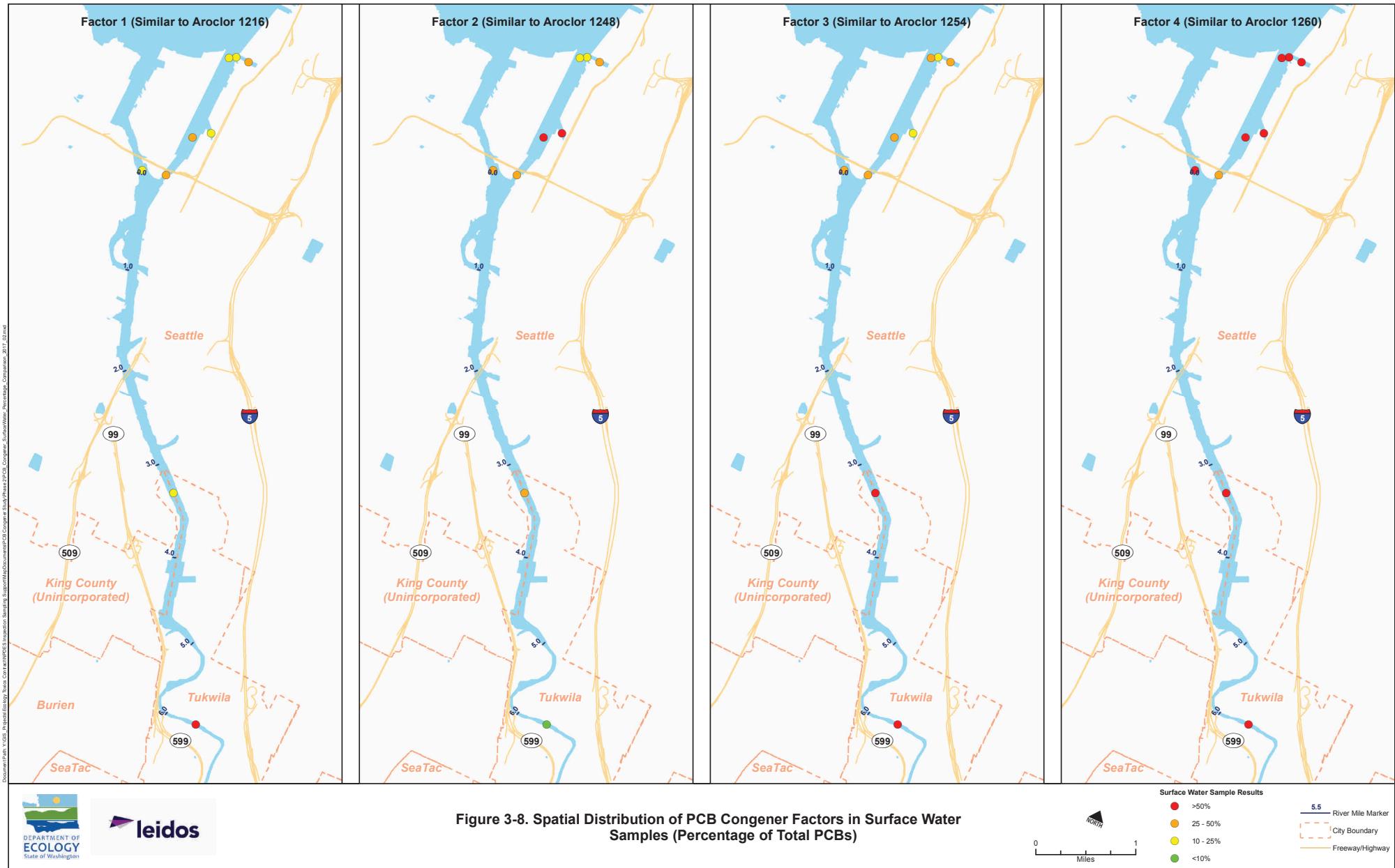


Figure 3-9. Mass-Weighted Average Contributions of Each Factor to the Sum of Modeled PCBs for the Surface Water Data Set by RM

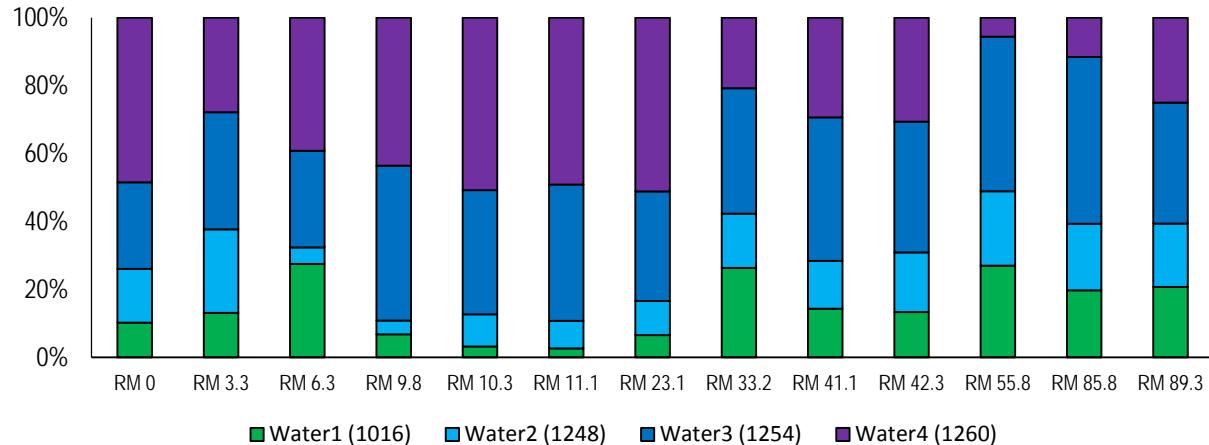
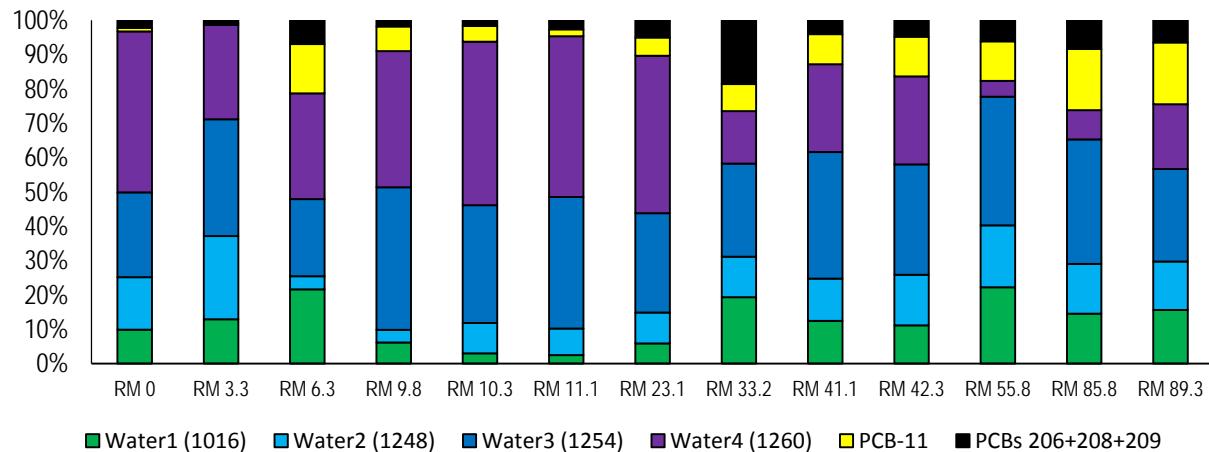


Figure 3-10. Mass-Weighted Average Contributions of the Four Factors Isolated from the Surface Water Data Set with the Inclusion of PCB-11 (yellow) and PCBs-206+208+209 (black)



Note:

The averages from RM 33.2 are affected by sample 681, which contained a high concentration (208 pg/L) of these three congeners.

PCB Congener Study Phase 2 - Source Evaluation

Non-Aroclor PCBs are more abundant in other systems. PCB-11 averages 3.6 pg/L in Green-Duwamish River surface water. The exact value of the average strongly depends on the treatment of non-detect values, which for purposes of calculating the averages below have been replaced with one-half the detection limit. In contrast, data available from STOrage and RETrieval (STORET—an electronic data system for water quality monitoring data developed by EPA) can be used to calculate the average concentrations of PCB-11 in other water bodies:

Location	Average Concentration of PCB-11
Portland Harbor Superfund site	231 pg/L
Upper Rio Grande River	101 pg/L
New York/New Jersey Harbor	108 pg/L
San Francisco Bay	108 pg/L
Delaware River (Du et al. 2008)	8.3 pg/L
Green-Duwamish River	3.6 pg/L

PCB-206, PCB-208, and PCB-209 average 234 pg/L in the Delaware River (Du et al. 2008), versus just 13 pg/L in the Green-Duwamish River; again, this average depends heavily on the treatment of non-detects.

3.4 Tissue

Studies Considered and Number of Samples

Study Code	Number of Samples Available	Column Used	Number of Samples Used in PMF Analysis	Number of Field Blanks
6	29	SPB-octyl	29	none
9	52	SPB-octyl	52	none
17	6	SPB-octyl	6	none
18	7	SPB-octyl	7	none
19	17	SPB-octyl	17	none
26	17	DB-5	17	none
Total Tissue Samples	128		128	none

All 128 samples were included in the PMF model.

Geographic Coverage

Tissue samples were collected in the East Waterway and the LDW; no tissue samples analyzed for the full suite of PCB congeners were identified in the Green River:

- 29 samples were collected from 17 locations in the East Waterway; and
- 99 samples were collected from 73 locations in the LDW.

Congeners

All studies used the SPB-octyl column; therefore, no compositing of congeners was necessary. Ninety congeners were included in the PMF model. Coeluting congeners in the tissue data set are listed below.

Coeluting Congeners in Tissue Data Set			
12+13	49+69	107+124	156+157
18+30	50+53	110+115	171+173
20+28	61+70+74+76	128+166	180+193
21+33	83+99	129+138+160+163	183+185
26+29	85+116+117	134+143	197+200
40+41+71	86+87+97+108+119+125	135+151+154	198+199
44+65+47	90+101+113	147+149	
45+51	93+95+98+100+102	153+168	

Detection Limits

LODs were provided for Study 6 only. All other LODs were estimated from the minimum detected concentration.

Uncertainty Matrix

RPDs of duplicates ranged from 2.4 to 48 percent. These were scaled using Equation 3.

Non-Detects

Only 1.4 percent of data points were BDL.

3.4.1 Number of Factors

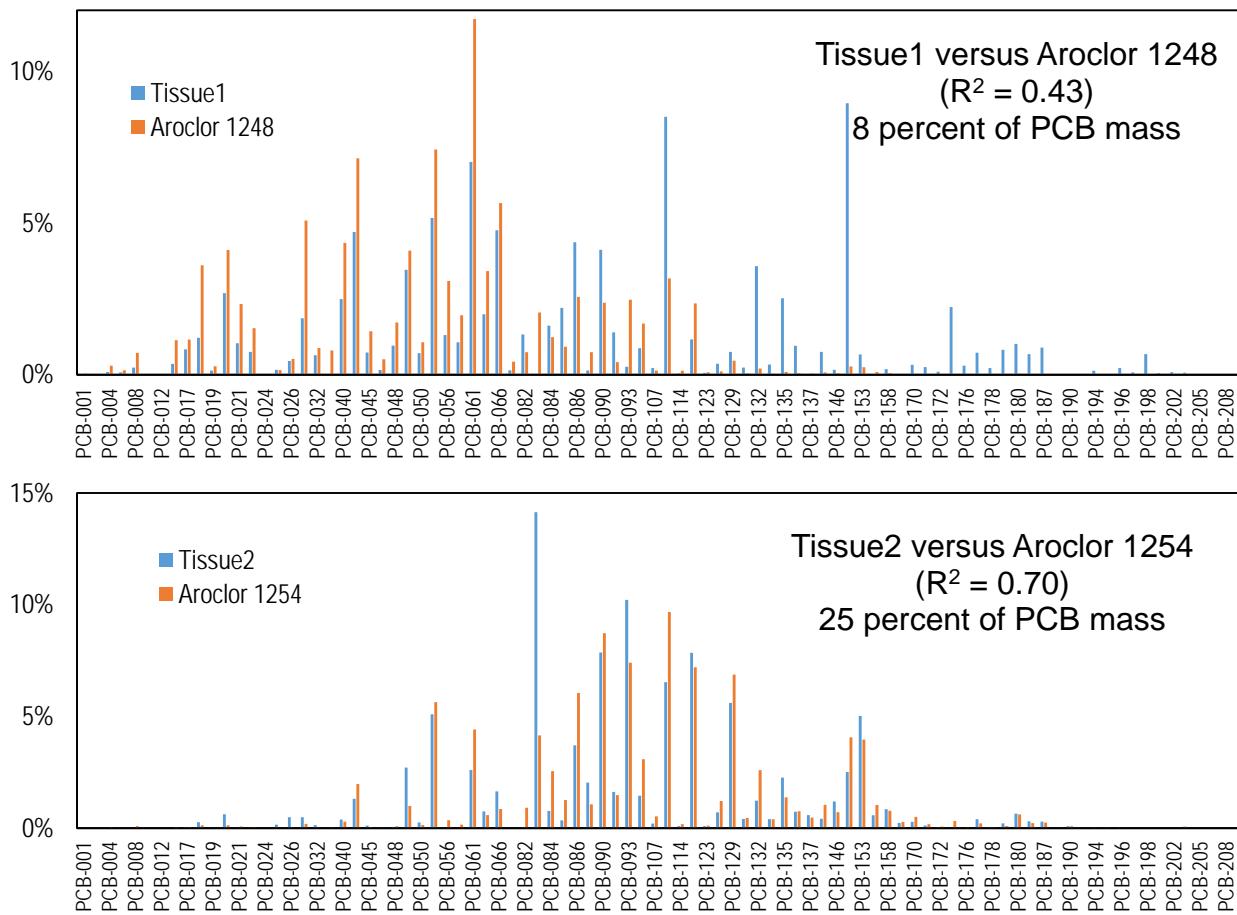
The five-factor solution was selected based on several criteria. Five was the highest number of factors that yielded a stable model solution. The RSD_G for 9 out of 10 seed runs was 0.6 percent. The agreement between the measured and modeled concentrations (R^2) was greater than 0.9 for 52 of the 90 peaks. Another 22 peaks yielded R^2 values greater than 0.8. A further eight peaks yielded R^2 values greater than 0.6. Peaks that were not well reproduced by the model were PCB-1 ($R^2 = 0.30$), PCB-3 ($R^2 = 0.07$), PCB-6 ($R^2 = 0.52$), PCB-11 ($R^2 = 0.15$), PCB-12 ($R^2 = 0.04$), PCB-194 ($R^2 = 0.49$), PCB-208 ($R^2 = 0.59$), and PCB-209 ($R^2 = 0.23$). PCB-11, PCB-12, PCB-208, and PCB-209 may be associated with pigments; therefore, it is not surprising that the PMF model may have difficulty modeling them because they come from different sources than most of the other peaks. The five-factor model was also interpretable.

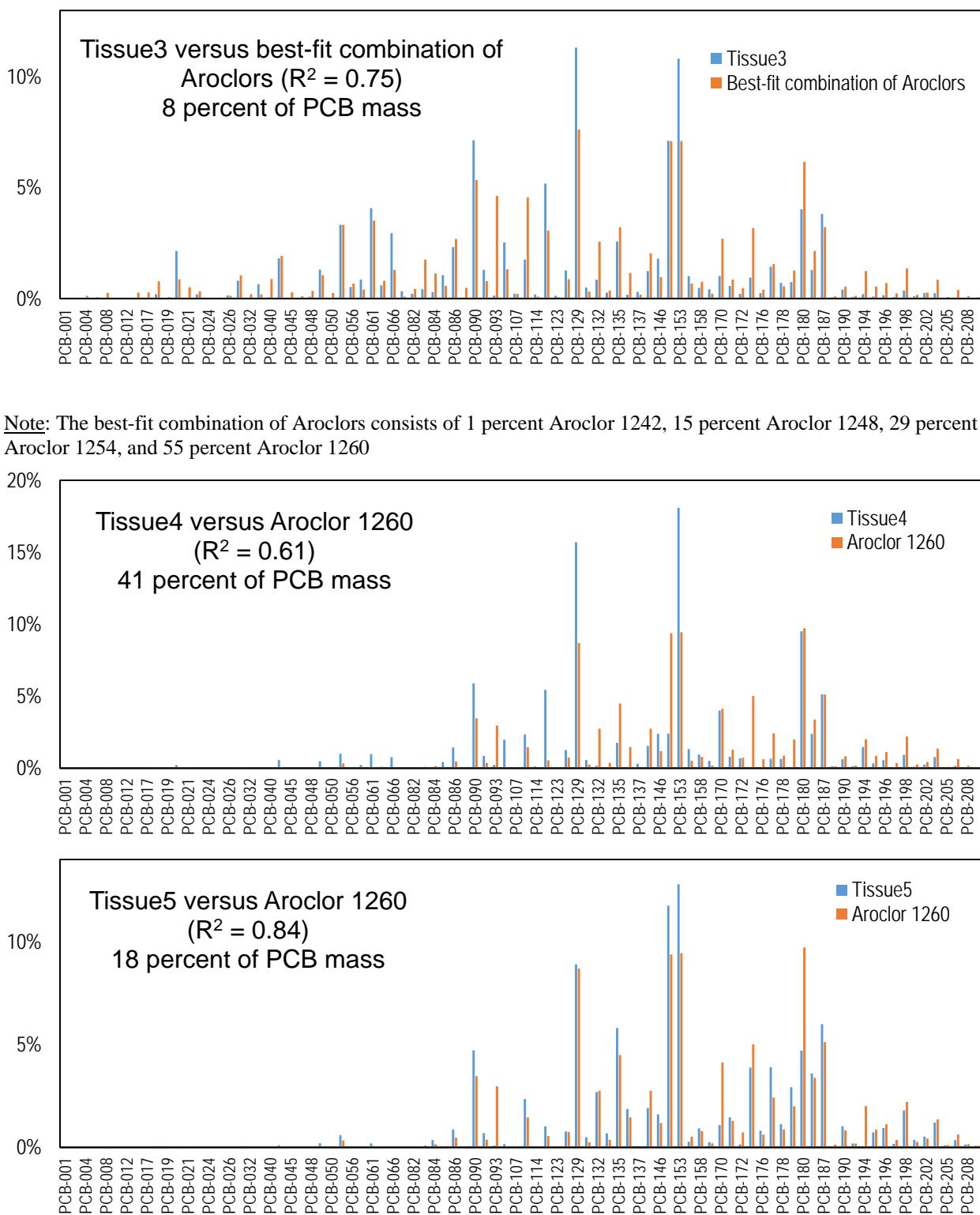
3.4.2 Factor Identification

Factor Tissue1 somewhat resembles Aroclor 1248 ($R^2 = 0.43$), although it contains more high molecular weight congeners than the Aroclor (Figure 3-11). This may suggest that Tissue1 represents weathered, higher molecular weight Aroclors such as Aroclor 1254. The best fit for Tissue1 as a combination of the four main Aroclors is 54 percent Aroclor 1248, 24 percent Aroclor 1254, and 22 percent Aroclor 1260, but even this best-fit profile only yields an R^2 value of 0.62.

PCB Congener Study Phase 2 - Source Evaluation

Tissue2 is similar to Aroclor 1254 ($R^2 = 0.70$). PCBs-83+99 are more abundant in Tissue2 than in the Aroclor. PCB-99 is considered a ‘group 2’ congener (Buckman et al. 2006) that has vicinal H-atoms exclusively in the ortho- and meta-positions in combination with two or more ortho-Cl substituents. These group designations suggest the bioaccumulation potential of the congeners, where group 1 congeners, such as PCB-153, have the highest probability of bioaccumulation and group 5 congeners have the lowest probability of bioaccumulation. This abundance of PCBs-83+99 may, therefore, indicate that Tissue2 represents Aroclor 1254 after some alteration via absorption, distribution, metabolism, and excretion (ADME) processes. The best fit for Tissue2 as a combination of the four main Aroclors is 99 percent Aroclor 1254 and 1 percent Aroclor 1242 ($R^2 = 0.70$), suggesting that Tissue2 represents Aroclor 1254 alone rather than a combination of Aroclors.

Figure 3-11. PCB Congener Fingerprints from Tissue Data Set

*PCB Congener Study Phase 2 - Source Evaluation***Figure 3-11 (Continued). PCB Congener Fingerprints from Tissue Data Set**Notes:

Coeluting groups of congeners are listed under the first congener in each group.

All 90 peaks are shown on graphs, but only 45 are labeled on the x-axis.

PCB Congener Study Phase 2 - Source Evaluation

Tissue3, Tissue4, and Tissue5 all somewhat resemble Aroclor 1260. This resemblance is strongest for Tissue5 (R^2 versus Aroclor 1260 = 0.84), which may indicate that Tissue5 represents a relatively unaltered Aroclor 1260 pattern.

Tissue3 resembles Aroclor 1260 slightly (R^2 = 0.55) but contains some lower molecular weight congeners than the Aroclor. This may indicate that it represents a mixture of Aroclors, and indeed, it is best explained as a mixture of 0.8 percent Aroclor 1242, 15 percent Aroclor 1248, 29 percent Aroclor 1254, and 55 percent Aroclor 1260 (R^2 = 0.75). This best-fit profile has some obvious discrepancies. PCBs-66, -90+101+113, -129+138+160+163, and -153+168 are more abundant in the factor than in the best-fit Aroclor profile, suggesting bioaccumulation and/or lack of degradation. Note that PCB-153 and PCB-129 are in groups 1 and 2, respectively.

PCBs-83+99, -93+95+98+100+102, -110+115, -132, -170, and -174 are more abundant in the best-fit Aroclor profile than in the factor, suggesting a lack of bioaccumulation and/or some degradation. PCB-98, PCB-99, PCB-110, PCB-132, and PCB-174 are all in groups 4 and 5, suggesting that they are comparatively more degradable than other PCB congeners. Therefore, Tissue3 probably represents a mixture of Aroclors that have undergone substantial alteration via ADME processes.

Tissue4 is also similar to Aroclor 1260 (R^2 = 0.61) and does not contain substantial amounts of any congeners that are not present in Aroclor 1260. Instead, it contains the same congeners as Aroclor 1260 but in different proportions. This suggests that Tissue4 represents Aroclor 1260 after substantial alteration via ADME processes. PCBs-105, -118, -129+138+160+163, and -153+168 are enhanced relative to Aroclor 1260, while PCBs-93+95+98+100+102, -132, 135+151+154, -136, -147+149, -174, and -179 are depleted relative to Aroclor 1260. PCB-129, PCB-138, PCB-163, and PCB-153 are in groups 1 and 2, while congeners PCB-95, PCB-98, PCB-135, PCB-151, PCB-136, PCB-148, PCB-174, and PCB-179 are in group 5.

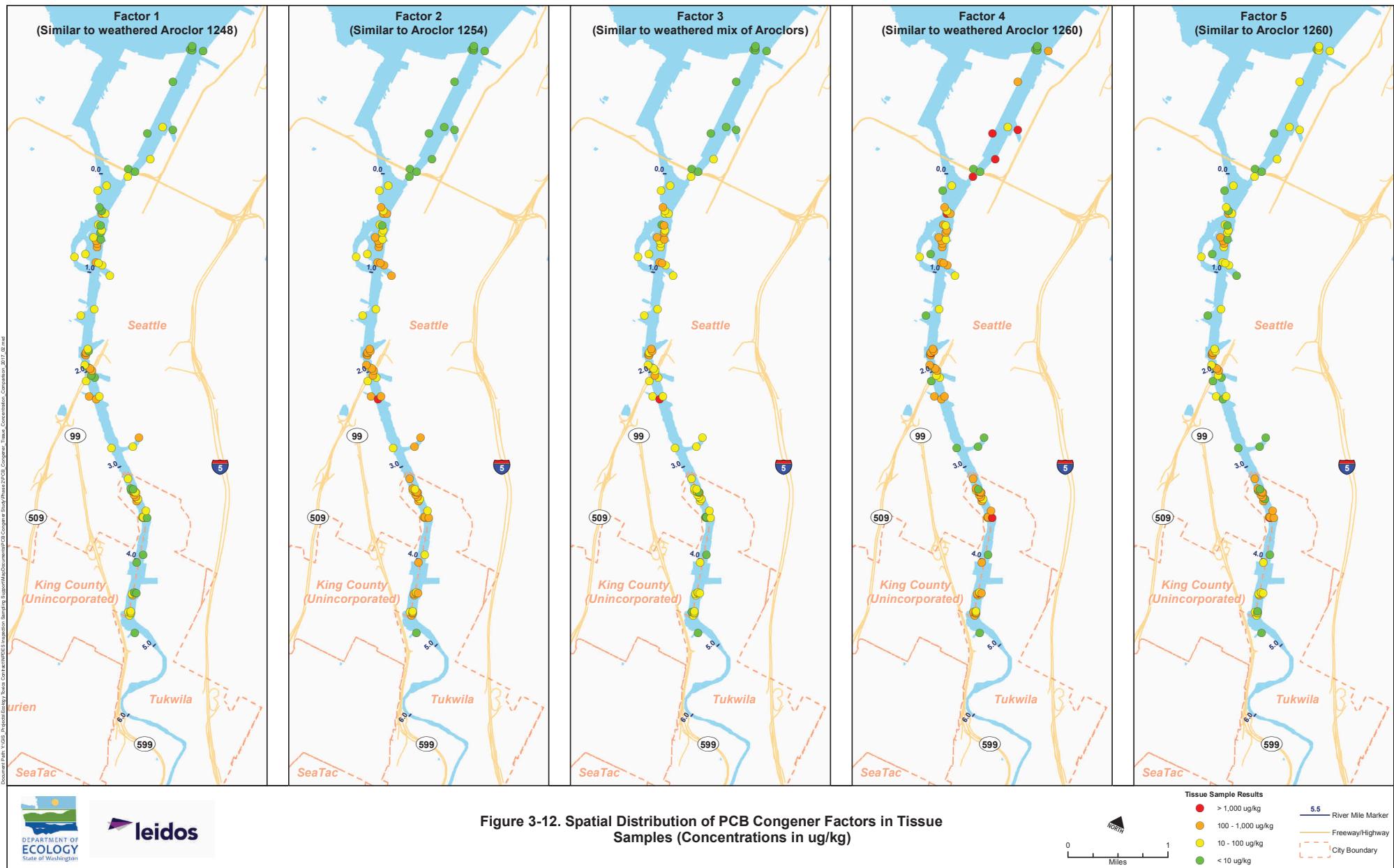
3.4.3 Spatial Distribution of Factors

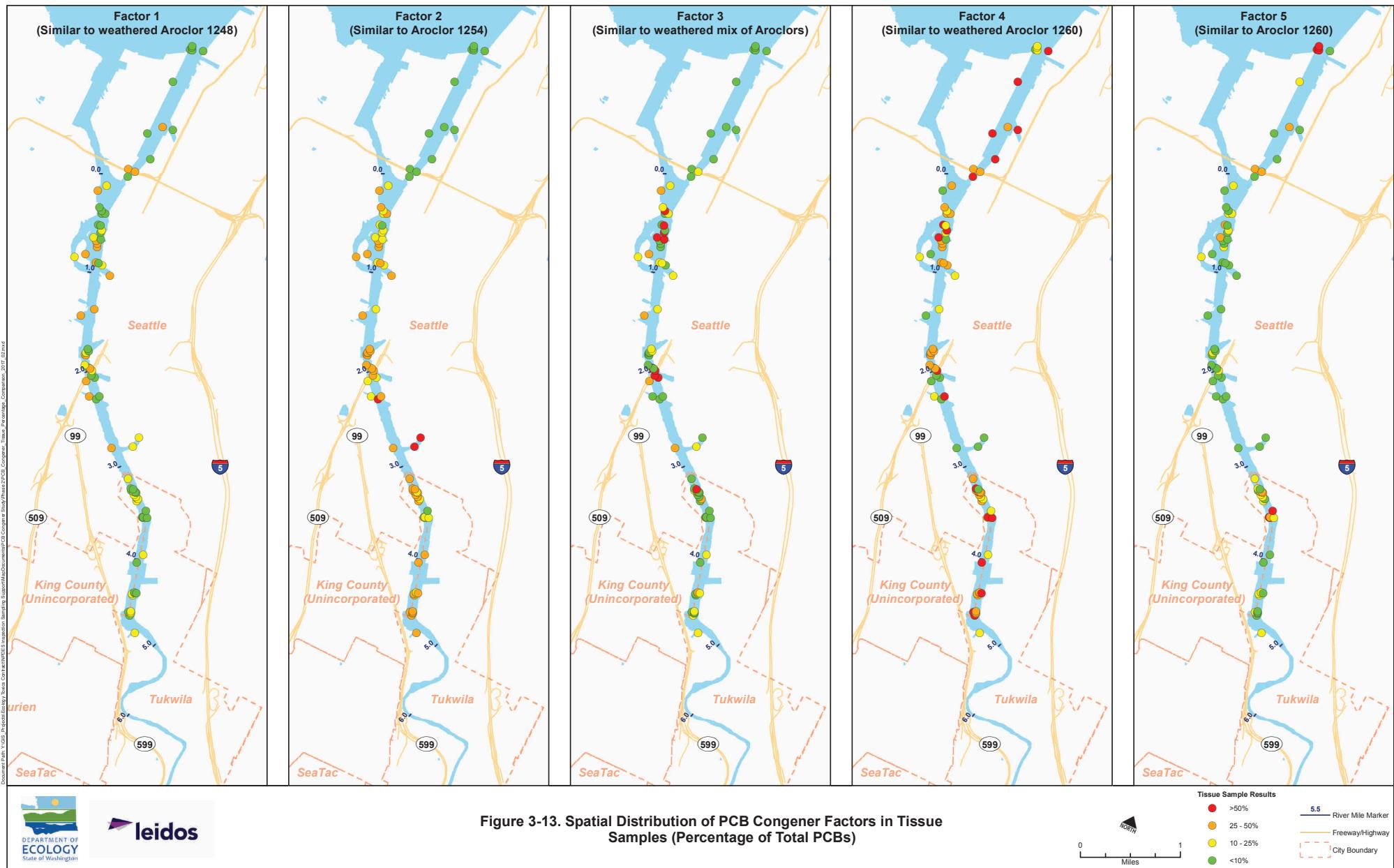
Tissue5 (weathered Aroclor 1260) is the most abundant factor at most locations, followed by Tissue2 (Aroclor 1254). The sediment analysis suggested that Sed5, which is strongly similar to Aroclor 1260, was dominant in the area east of Harbor Island. The tissue results are in agreement with this—Tissue4 and Tissue5, which both appear to be derived from Aroclor 1260, dominate at this location.

The spatial distribution of the tissue factors is displayed by concentration in Figure 3-12 and by fraction of total PCBs in Figure 3-13. More detailed maps of the spatial distribution of tissue factors are provided in Appendix B.

3.4.4 Comparison to Other Systems

The Hanford site in Washington State was similarly impacted by high molecular weight PCB formulations. PCBs in the fish there displayed two fingerprints that were similar to Aroclor 1260, with one appearing to be more weathered than the other (Rodenburg et al. 2015b). It is not surprising that the two fingerprints that were most similar to Aroclor 1260 from the Hanford site and the Green-Duwamish Waterway are similar to each other. However, it is somewhat surprising that the two fingerprints from these waterways, which represent the more weathered versions of Aroclor 1260, are also very similar to each other, with a correlation coefficient (R^2)





PCB Congener Study Phase 2 - Source Evaluation

of 0.91. This is especially surprising given that the Hanford site is a freshwater ecosystem, while the LDW is estuarine.

3.4.5 Factor Abundance by Species

There are notable differences in the abundance of each tissue factor by species. In Figure 3-14, the species are grouped as benthic, fish, and shellfish species. (Note that amphipods are somewhat arbitrarily included in the benthic category.) Fish and shellfish are more likely to accumulate Tissue4, the weathered Aroclor 1260 factor. Brown rockfish, in particular, appear to bioaccumulate Tissue4 almost exclusively. Because Tissue5 represents a relatively unweathered Aroclor 1260 pattern, while Tissue4 is a weathered Aroclor 1260 pattern, this may indicate that brown rockfish are relatively efficient at altering the PCB pattern via ADME processes. In contrast, a high proportion of the PCBs accumulated by geoduck are in the form of Tissue5, the largely unweathered Aroclor 1260, perhaps indicating that they are not very efficient at altering the PCB congener fingerprint via ADME processes. It is important to note, however, that some of the differences in PCB fingerprints across species may result from location and not from ADME processes.

3.5 Storm Drains

Studies Considered and Number of Samples

Study Code	Sample Type	Number of Samples Available	Column Used	Number of Samples Used in PMF Analysis	Number of Field Blanks
20	Storm drain water	15	SPB-octyl	14	none
21	Storm drain water	25	DB-5	25	
21	Storm drain solids	30	DB-5	30	
22	Storm drain water	1	DB-5	521	none
22	Storm drain solids	4	DB-5	4	none
Total Storm Drain Samples		75		74	none

Of the 75 samples, 1 was discarded (sample 1589) because 65 of the targeted 73 congeners were BDL.

Geographic Coverage

The 74 samples used in the PMF analysis were collected from 64 locations spread throughout the LDW. No relevant samples from upstream or downstream of the LDW were identified.

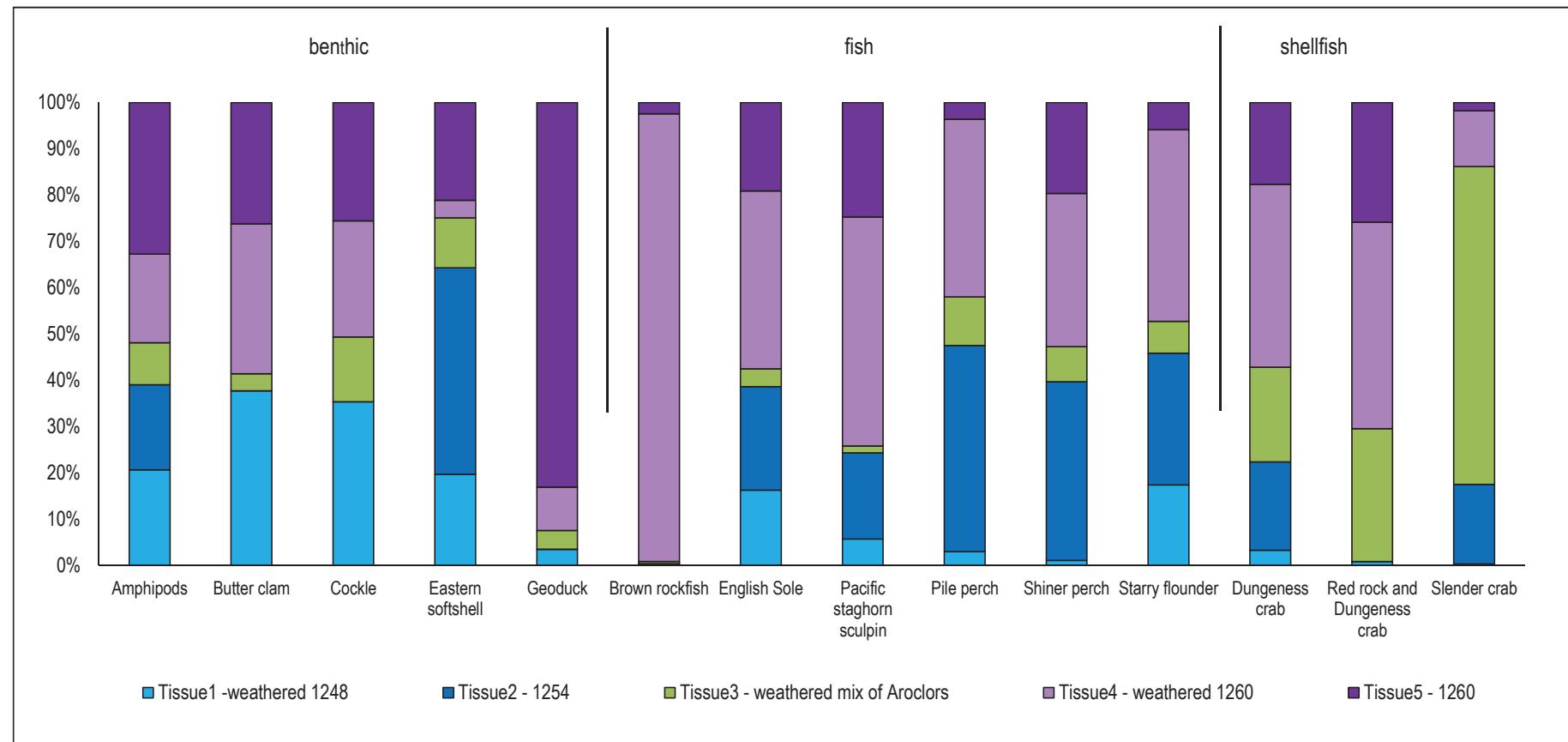


Figure 3-14. Abundance of Tissue PMF Factors by Species

Congeners

Congeners were composited across DB-5 and SPB-octyl columns. Seventy-three peaks were included in the model. Coeluting congeners in the storm drain data set are listed below.

Coeluting Congeners in Storm Drain Data Set			
4+10	50+53	93+95+98+100+102	153+168
12+13	56+60	107+109+124	156+157
16+32	61+66	110+111+115	171+173
20+21+28	83+99	128+162+166	180+193
26+29	84+92	129+138+158+160+16 3+164	183+185
40+41+64+71+72	85+86+87+97+108+11 2+116+117+119+125	132+161	196+203
44+47+65	88+91	134+139+140+143+14 6+147+149+165	197+200
45+51	90+101+113	135+151+154	198+199

Detection Limits

LODs were provided for all data.

Uncertainty Matrix

RPDs of duplicates ranged from 10 to 51 percent. These were scaled using Equation 3.

Non-Detects

Approximately 15.3 percent of data points were BDL.

3.5.1 Number of Factors

The PMF2 analysis of the storm drain matrix yielded six factors. This number of factors was chosen based on several criteria. First, six was the highest number of factors that yielded a stable solution, with an RSD_G for the 10 seed runs of 0.6 percent. Second, the six-factor solution accurately reproduced the data. The agreement between measured and modeled concentrations (R^2) was greater than 0.9 for 65 of the 73 peaks analyzed. Another five peaks yielded R^2 values greater than 0.8. The peaks that were not well described by the model were PCB-1 ($R^2 = 0.61$), PCB-3 ($R^2 = 0.49$), and PCB-4 ($R^2 = 0.68$). Third, the six-factor model produced factors that were interpretable.

3.5.2 Factor Identification

Four of the six factors closely resembled Aroclors ($R^2 > 0.85$) (Figure 3-15). The remaining two factors contained relatively high proportions of non-Aroclor congeners. In factor Storm6, the sum of PCB-206, PCB-208, and PCB-209 comprised 11 percent of the total PCBs. Even without these congeners, factor Storm6 did not resemble any Aroclor ($R^2 < 0.2$), nor any linear combination of Aroclors ($R^2 < 0.22$). Storm6, therefore, likely represents PCBs arising from or associated with titanium dioxide and/or phthalocyanine pigments. Factor Storm3 contained 13 percent PCB-11. When PCB-11 is excluded from the correlation, Storm3 resembles Aroclor

PCB Congener Study Phase 2 - Source Evaluation

1260 ($R^2 = 0.78$). It best resembles a mixture of 7 percent Aroclor 1242, 34 percent Aroclor 1254, and 58 percent Aroclor 1260. Thus, it is probably best described as an integrated mixture of many PCB sources, with influence from organic pigments.

The storm drain sample matrix contains both storm drain water and storm solids samples. Storm1, which is similar to Aroclor 1016 and has the lowest average molecular weight of the six factors, is more abundant in the storm drain water samples than in the storm solids samples. This is not surprising because Storm1 is more likely to be in the dissolved phase due to its low molecular weight.

Figure 3-15. PCB Congener Fingerprints from Storm Drain Data Set

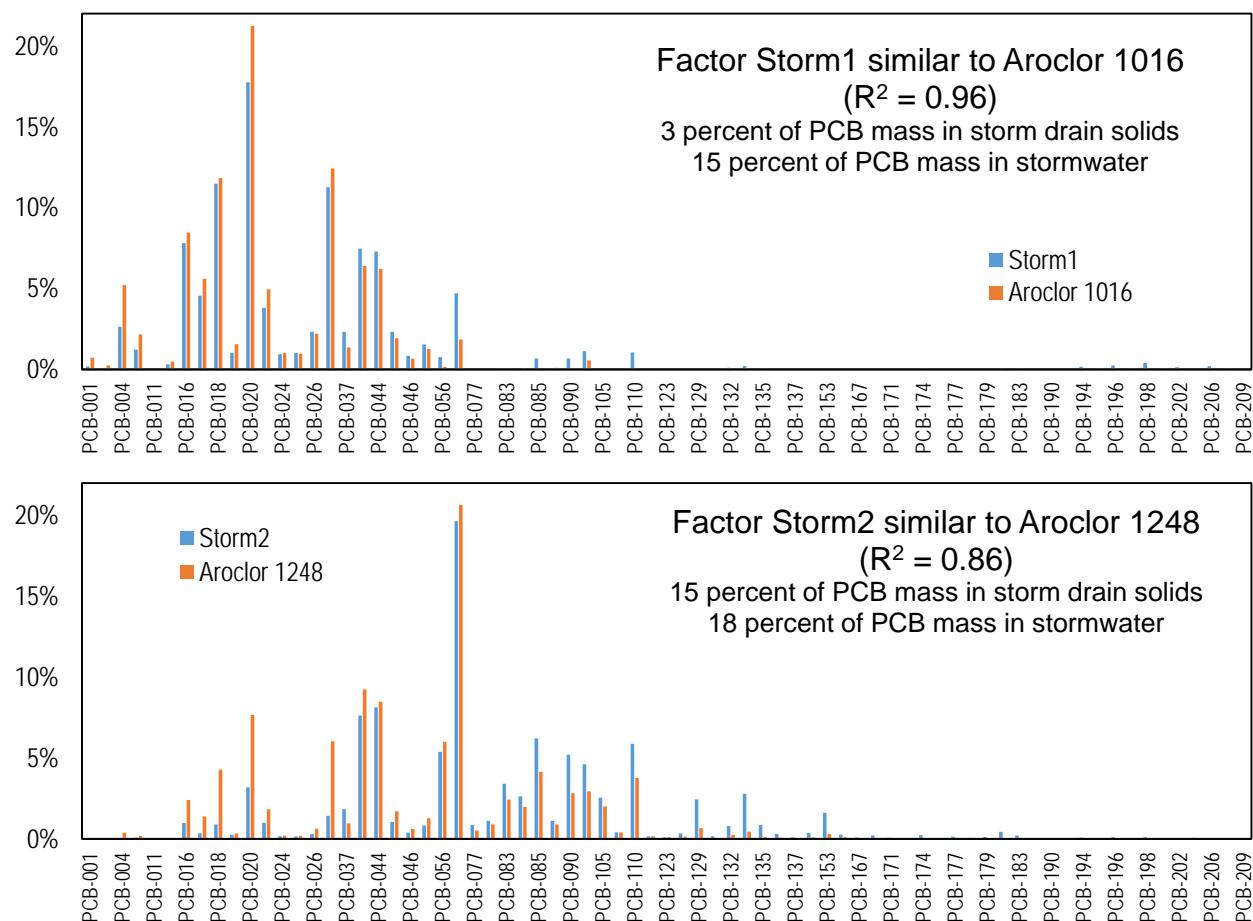
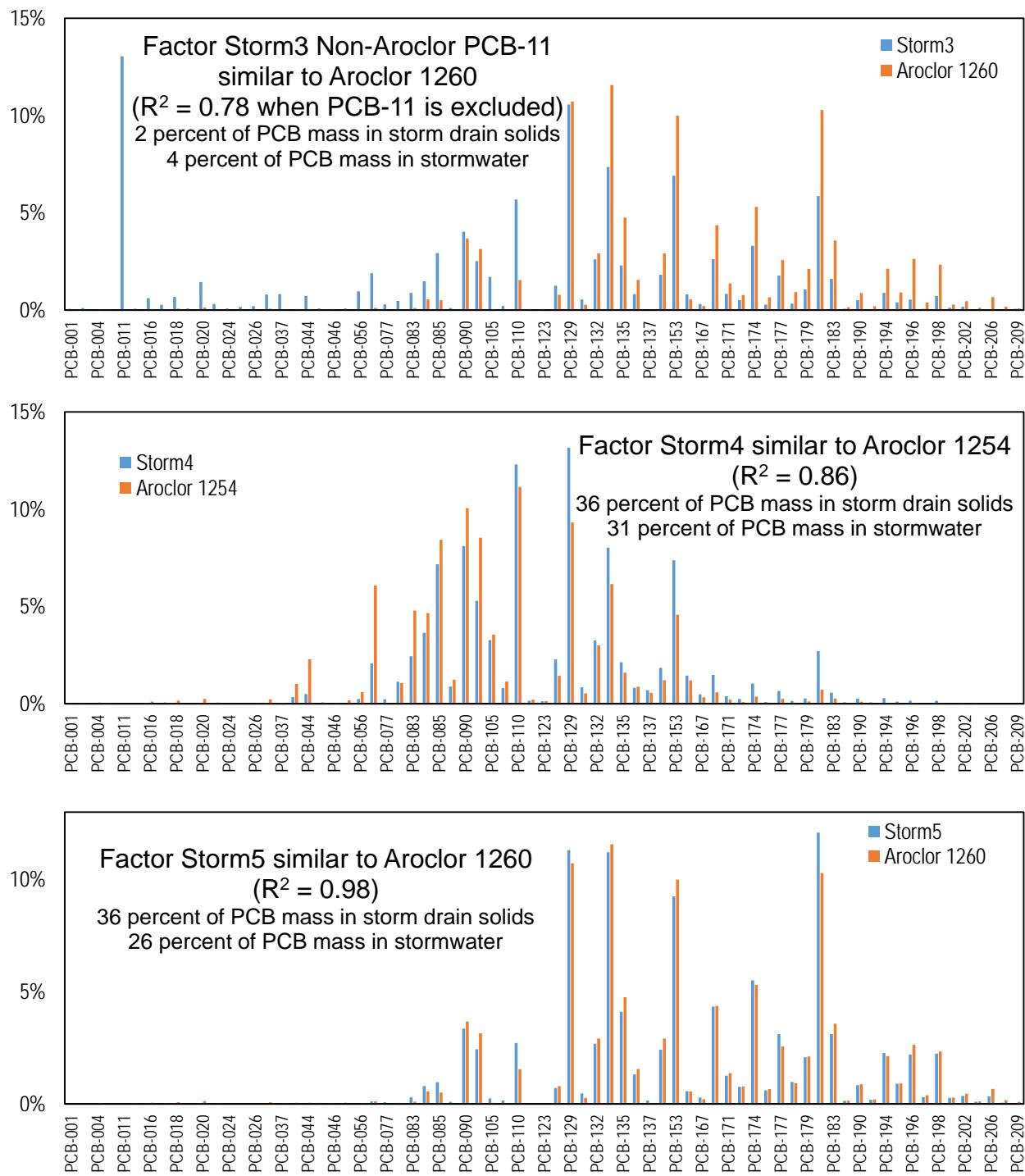
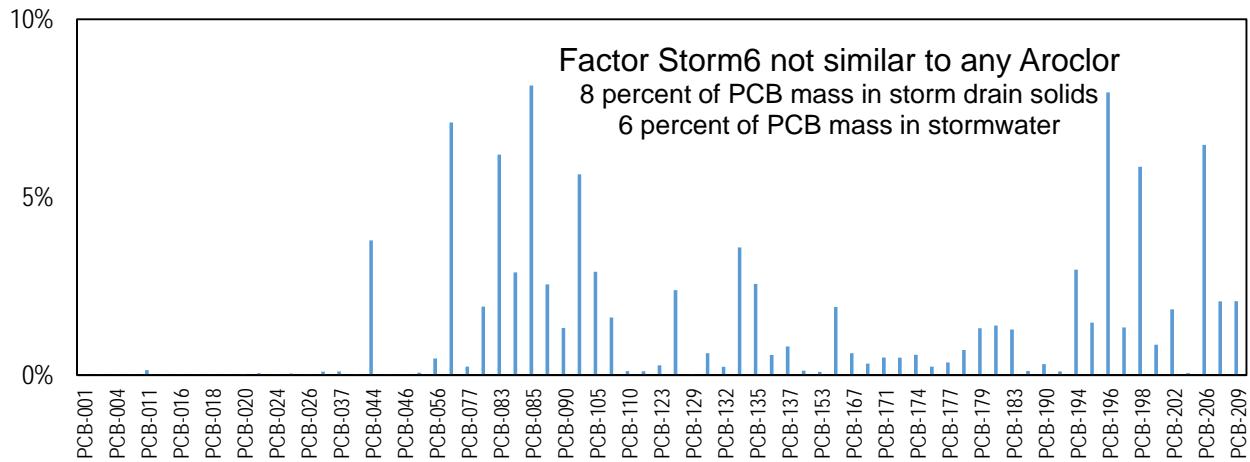


Figure 3-15 (Continued). PCB Congener Fingerprints from Storm Drain Data Set

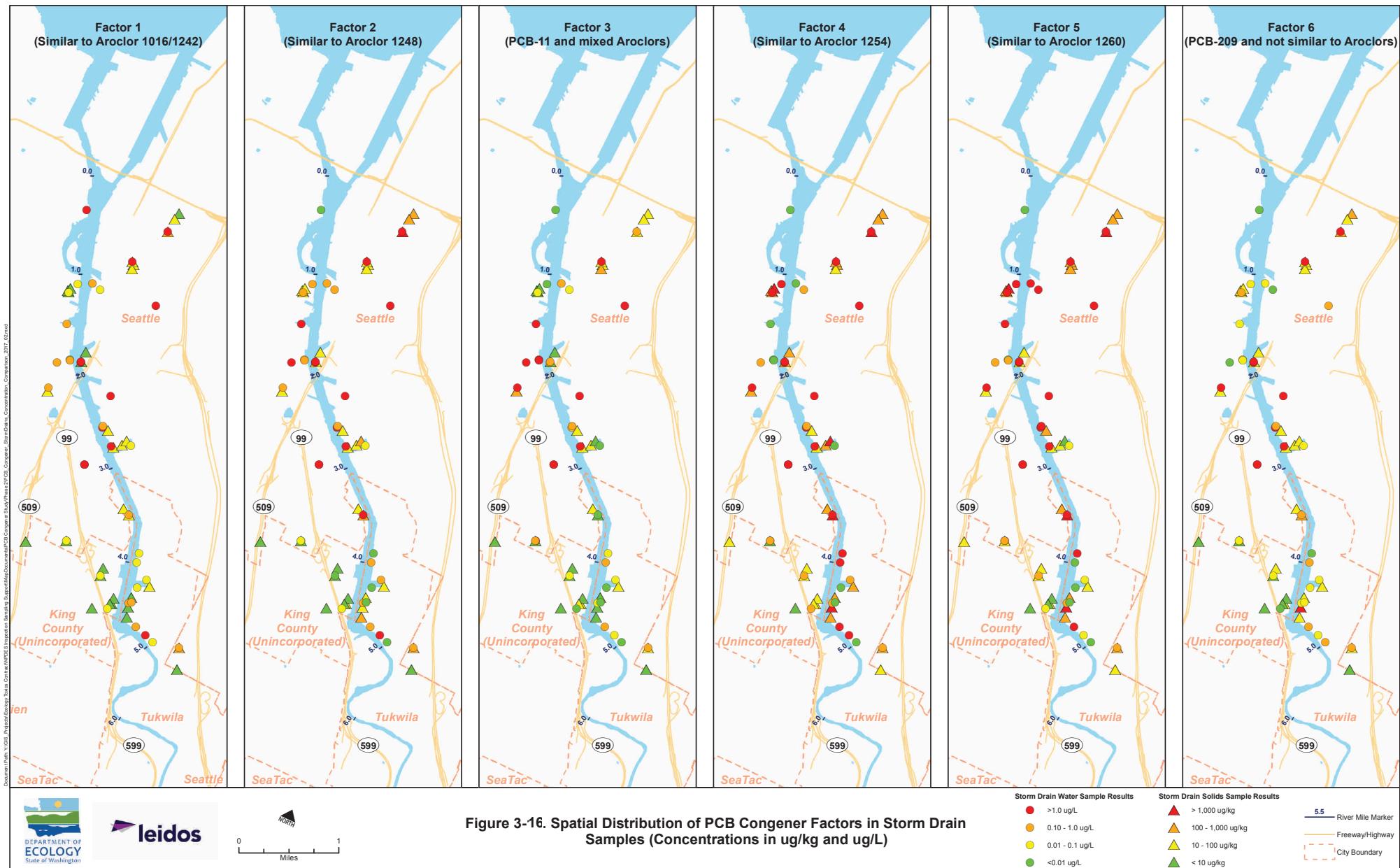
*PCB Congener Study Phase 2 - Source Evaluation***Figure 3-15 (Continued). PCB Congener Fingerprints from Storm Drain Data Set**Notes:

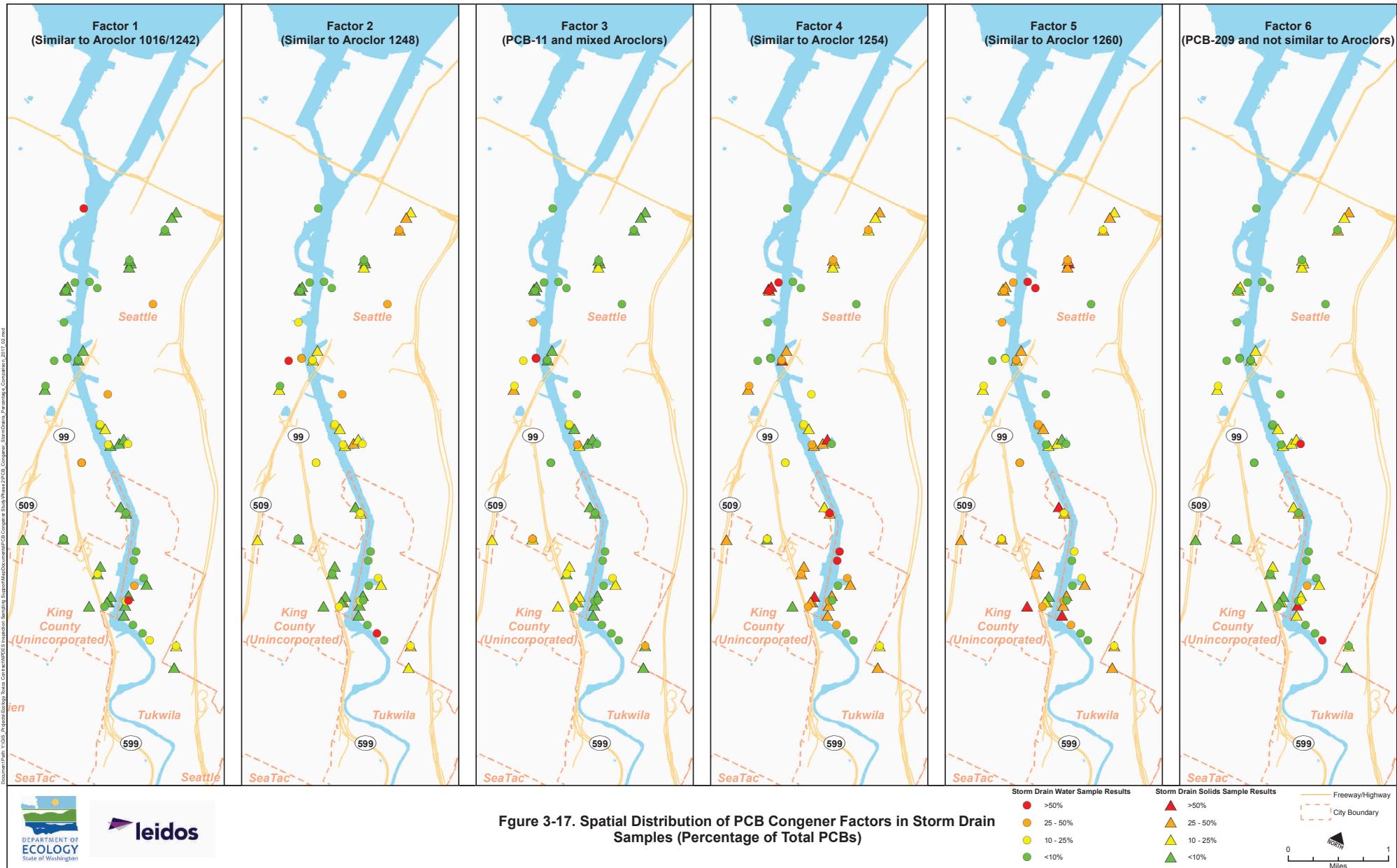
Coeluting groups of congeners are listed under the first congener in each group.

All 80 peaks are shown on graphs, but only 40 are labeled on the x-axis.

3.5.3 Spatial Distribution of Factors

The spatial distribution of the storm drain factors is displayed by concentration in Figure 3-16 and by fraction of total PCBs in Figure 3-17. Most of the mass of PCBs in the storm drain samples consists of Storm2 (Aroclor 1248), Storm4 (Aroclor 1254), and Storm5 (Aroclor 1260). These three factors are relatively evenly distributed across the study area. In contrast, the factors that are associated with pigment sources (Storm3 and Storm6) dominate at a small number of locations, perhaps indicating discrete sources. More detailed maps showing the spatial distribution of storm drain factors are provided in Appendix B.





PCB Congener Study Phase 2 - Source Evaluation

4.0 Modeling Uncertainty

The PMF analysis described in this report is very reproducible (i.e., when the PMF2 program is used to analyze the same data set multiple times using different seed values, the results are typically within approximately 5 percent relative standard deviation). This is one of the criteria used to select the optimal number of factors (i.e., the optimal model solution). This model stability seems to imply a low level of uncertainty in the modeling exercise as a whole; yet, there are many sources of uncertainty that are less visible, including:

- Insufficient data (not enough samples or detected analytes).
- Different models may give different results for the same data sets.
- Various permutations of the same data set may give different model results, even when the same model is used.
- Choosing a sub-optimal number of factors.
- Factors may be misinterpreted.

These sources of uncertainty are detailed below.

4.1 Insufficient Data

The common wisdom is that data sets for PMF analysis should have either more samples than analytes or at least an equal number of samples and analytes. This is because PMF is a physical-statistical model; therefore, data sets with many more analytes than samples will cause the solution to be unstable (i.e., a small number of samples cannot contain enough information to constrain the solution for a large number of analytes). In the present study, this became an issue for the air (atmospheric deposition) matrix. Because only 64 samples (some of which were duplicates of other samples) were available, only 64 analytes (PCB peaks) could be included in the data matrix. Despite this, those 64 peaks described about 88 percent of all the PCB mass detected in the atmospheric deposition samples.

Insufficient data are particularly problematic when the available data do not provide adequate spatial coverage of the study area. The surface water data, for example, include very few samples from the LDW; therefore, no conclusions can be drawn about sources of PCBs to the water of the LDW.

Insufficient data can also yield misleading conclusions about pollution sources when there are not enough data points to accurately represent the environmental compartment from which they are taken. This is most problematic when the compartment is likely to be influenced by a wide variety of pollution sources/processes and/or is difficult to sample. In the present study, tissue is an example of a matrix that is difficult to sample (because the targeted species cannot always be caught) and is likely subject to the same number of PCB sources as surface water or sediment but is likely influenced by additional processes (i.e., ADME processes that differ by species). For these reasons, the tissue PMF results should be interpreted carefully.

Insufficient data are also a problem when a large number of samples have been collected, but the analytes are frequently BDL. Samples in which very few analytes were detected generally must be discarded from the PMF input. Similarly, analytes (PCB peaks) that are BDL in a majority of

samples are usually discarded from the PMF input. This can leave behind a small number of data points and/or PMF input in which there is a large proportion of BDL values, which can yield PMF results that are unstable (i.e., the RSD_G is high). This was the case with the surface water data.

4.2 Different Models May Give Different Results When Analyzing the Same Data Set

EPA's PMF 5.0 was originally intended to be used for this analysis because it is publicly available and was developed by EPA for this type of pollution source evaluation. All of the data sets described herein were analyzed via PMF 5.0; unfortunately, many of them yielded no stable solution in the PMF 5.0 analysis (i.e., the model did not converge on a solution). For the data sets that did converge on a solution, PMF 5.0 and PMF2 generally indicated the same optimal number of factors, but the fingerprints produced by PMF 5.0 were noticeably different from those produced by PMF2. Experts in using PMF 5.0 have confirmed that these data sets were challenging for the PMF 5.0 model (Rodenburg 2017).

The factors generated from the PMF2 analysis generally represent Aroclors. In contrast, the factors generated from the PMF 5.0 analysis do not. As discussed in Section 2.3, neither the operator nor the PMF model is in any way biased toward ‘finding’ Aroclor-type patterns. To the extent that the PMF model does generate fingerprints that resemble Aroclors, they result from PCB congener concentrations that vary in patterns indicative of Aroclors. This is to be expected because Aroclors can reasonably be anticipated to be the dominant PCB sources in the United States.

Several experts in PMF modeling were consulted to determine the source of this discrepancy and a way to counteract it. Dr. Gary Norris of EPA’s National Exposure Research Laboratory noted that PMF 5.0 has a high number of ‘swaps’ relative to PMF2. Swaps occur when, during bootstrapping (resampling the data set and re-running the PMF 5.0 analysis), “factors change so much that they exchange identities, indicating a ‘not-well-defined solution’” (Brown et al. 2015). He noted that PMF 5.0 had not been evaluated for the type of data this project is analyzing, and that when even 1 of the default of 20 seed runs does not converge in PMF 5.0, the results should not be interpreted. Thus, for this project, none of the results obtained from PMF 5.0 should be considered useful. Dr. Norris suggested that a different model be used. He evaluated the sediment data using a model under development at EPA called Unmix Optimum (abbreviated as UnmixO) and found similar source fingerprints to those generated by PMF2. Currently, UnmixO is not publicly available.

As a result, efforts to use PMF 5.0 for this study were abandoned, and PMF2 was used instead. Confidence can be placed in the PMF2 results because PMF2 found a stable solution for all five environmental compartments, produced factors that resembled Aroclors, and produced factors that matched across environmental compartments, thus telling a coherent story about PCB contamination in the Green-Duwamish River basin across all five media. Nevertheless, the failure of PMF 5.0 in this project suggests that all such factor analysis must be approached with caution. Most importantly, the results of factor analysis must be consistent with all other knowledge about pollutant (in this case, PCB) sources and processes in the system. The PMF2 results are consistent with this knowledge, while the PMF 5.0 results are not.

4.3 Various Permutations of the Same Data Set May Give Different Model Results

A robust PMF solution depends on high-quality-assured input data sets, appropriate ways to treat uncertainties and BDL measurements, and careful PMF model parameter settings (Paatero and Tapper 1994; Reff et al. 2007). All of the environmental compartments analyzed here were investigated using various permutations of the data sets in which the model settings and parameters varied. These permutations included:

- Excluding data (samples or analytes),
- Changing the uncertainty matrix,
- Changing the LODs matrix, and
- Changing the proxy values used in place of values that are BDL.

Analysis using various permutations was sometimes intentional, but more often, was done because the information about quality assurance (QA) parameters such as detection limits, surrogate recoveries, and duplicate samples became available in a piecemeal fashion during the project. As a result, several preliminary data sets were tried before the final QA data became available. Even when all QA data are immediately available, PMF analysis is typically an iterative process, in which the user starts with the largest reasonable data set and then deletes analytes or samples that seem to be causing instability in the model solution until a final solution emerges that is stable and interpretable (i.e., as noted above, the solution must be consistent with the existing knowledge about the system). This approach is useful because it allows the user to verify that the PMF solution is similar across many different permutations of the input data sets. However, this approach also necessarily means that there is a certain amount of operator bias in the solution. Different operators may reach slightly different model solutions. However, the knowledge that several permutations of each data set converge on very similar solutions that tell the same basic story about PCB contamination in the Green-Duwamish River basin lends confidence that the solution and conclusions drawn from it are valid.

As noted above, in analyzing many permutations of the same data set, one of the main goals is to find a stable solution (i.e., one in which multiple seed runs give essentially the same result, as measured by a low RSD of the ‘G’ matrix [RSD_G]). Experience with other data sets, as well as literature on PMF (Paatero and Tapper 1994; Reff et al. 2007), suggest that all of the issues listed above can cause high RSD_G: inaccurate estimates of uncertainty, high numbers of BDL values, inaccurate LODs (which affect both the LOD matrix and the proxy values used for BDL concentrations), and samples/analytes that are significant outliers (i.e., that do not vary in the same patterns as the other samples/analytes). The iterative approach to finding a suitable model solution focuses first on adjusting the uncertainty matrix because many reasonable values for the uncertainty matrix are possible (Reff et al. 2007). In this source evaluation, the uncertainty matrix was adjusted as described in Section 2.2. The uncertainty matrix was judged to be acceptable when it produced stable model solutions (i.e., the 10 seed runs agreed with each other).

Second, LODs may be adjusted. This is justifiable in the present work because LODs were frequently not provided and, therefore, had to be estimated from the minimum detected concentrations. As a last resort, samples/analytes may be removed because they appear to be

outliers or have large numbers of BDL values. When samples or analytes are removed, it is necessary to try to determine why they vary according to different patterns more than the other samples/analytes, because the answers may provide useful information about PCB sources or processes.

For example, the surface water data set was analyzed with the 42 congeners shown in Figure 3-6, as well as PCB-11, PCB-77, and PCB-156. These three congeners were not well described by the resulting model, and the overall stability of the model (RSD_G) was poor for all of the numbers of factors investigated. These three congeners were, therefore, excluded and the model was re-run, resulting in a stable solution when four factors were requested. It is not surprising that these three congeners would be poorly described by the model. In the case of PCB-11, this is because it was below detection in more than one-half of all surface water samples and because it arises from different sources (pigments) relative to the other PCBs. PCB-77 and PCB-156 are dioxin-like congeners that could be produced during incineration (Jansson et al. 2011), which could explain why they were not well described by the PMF model. In addition, these two congeners were BDL in approximately one-third of all samples.

4.4 Choosing a Sub-Optimal Number of Factors

PMF experiences the same difficulties in determining the optimal number of factors as all other forms of factor analysis. It is important to choose the ‘best’ number of factors that provides clear, physically meaningful results (Reff et al. 2007). On the one hand, more factors are preferable in that they reveal more information about sources and processes. On the other hand, too many factors can result in generation of more than one factor that describes the same source/process, or factors that are not meaningful (i.e., ‘over-fitting’). An advantage of the PMF 5.0 software is that it includes bootstrapping and displacement routines that help the user identify the best number of factors (Norris et al. 2014; Brown et al. 2015). PMF2 does not have this feature and, therefore, the choice of the correct number of factors is somewhat more difficult.

Section 2.4 described the four criteria used to identify the optimal number of factors. Even when all of these criteria are considered, it can be difficult to identify the optimal number of factors. In the present work, the number of factors was relatively obvious for the air (atmospheric deposition), sediment, tissue, and storm drain compartments. For these compartments, the optimal number of factors was the highest number of factors that yielded a low RSD_G (less than 1 percent for air, tissue, and storm drains, and approximately 6 percent for sediment). In all four cases, this number of factors produced a solution in which most of the fingerprints resembled Aroclors. For air, sediment, and storm drain compartments, the optimal number of factors did not result in more than one factor similar to the same Aroclor.

For the tissue compartment, the optimal number of factors did produce two fingerprints that were similar to Aroclor 1260, but this outcome is judged to be reasonable because (1) the two fingerprints were not similar to each other, (2) a similar set of fingerprints was observed in fish tissue from the Hanford site (Rodenburg et al. 2015b), and (3) biological tissues are subject to additional processes affecting the PCB fingerprints. In this case, one of the Aroclor 1260 fingerprints was thought to resemble the unweathered Aroclor, and the other was thought to represent Aroclor 1260 after extensive alteration via ADME processes. The Hanford site is a relevant comparison because it is similarly impacted by high molecular weight PCB

PCB Congener Study Phase 2 - Source Evaluation

formulations, and the tissue samples from the Hanford site were measured using very similar methodology (Rodenburg et al. 2015b).

The optimal number of factors was less apparent for the surface water compartment, likely because of the large number of BDL values in the surface water data set, which necessitated limiting the analyte list to just 42 peaks with a total of 30 percent of all data points BDL. To address this form of uncertainty in the surface water compartment, additional data collection is needed, where possible obtaining detections instead of non-detects. For surface water, seven factors yielded a stable solution (low RSD_G), but three of the seven factors were not significant in the multiple linear regression of the ‘G’ matrix versus the sum of PCBs. Many of these seven factors did not resemble Aroclors. Also, the model fit was not significantly better for the seven-factor model relative to the four-factor model.

4.5 Factors May be Misinterpreted

There are several ways in which the operator can influence the PMF solution, but the greatest influence comes after the PMF analysis is complete, as this is when the PMF output must be interpreted (Reff et al. 2007). As noted in Section 2.5, in the case of PCB analysis, the advantage of *a priori* knowledge about PCB sources exists—the primary PCB sources in the United States are Aroclors. The Aroclors were produced by Monsanto, the only North American producer of PCBs, supplying about 99 percent of the domestic market (EPA 1976). Although PCBs can also be produced inadvertently during some chemical processes, these sources are thought to be small relative to the amount of Aroclor PCBs produced and used in the United States. The PMF solution should, therefore, include factors that resemble Aroclors. For this reason, the factors generated by the PMF analysis were compared with single Aroclors and mixtures of Aroclors (see Section 2.5).

In some cases, identifying factors is unambiguous. For example, all five environmental compartments yielded a factor that was strongly similar to Aroclor 1260, with the agreement (R^2) between the fingerprint and the measured Aroclor 1260 profile ranging from 0.84 (tissue) to 0.99 (sediment). One can confidently assert that these factors represent Aroclor 1260 and that they have undergone minimal weathering. In other cases, identifying factors, even when they resemble Aroclors, is less certain. For example, the storm drain compartment produced a factor that somewhat resembled Aroclor 1248, but the agreement (R^2) was only 0.43. This leads to several questions: Does this factor represent weathered Aroclor 1248? Does this factor represent weathered Aroclor 1254 or 1242? Does this factor represent a mixture of Aroclors?

In this study, the PMF fingerprints have been compared with both the individual Aroclors and the best-fit mixture of Aroclors from Equation 1. When the agreement between the fingerprint and a single Aroclor is greater than approximately 0.8, the factor was considered to represent an unweathered single Aroclor. When the agreement was not as good (i.e., R^2 between approximately 0.4 and 0.8), the factor was interpreted as representing a weathered Aroclor. In only one case was a PMF fingerprint observed that was well-described as a mixture of Aroclors—Tissue3 resembled a mixture of 1 percent Aroclor 1242, 15 percent Aroclor 1248, 29 percent Aroclor 1254, and 55 percent Aroclor 1260 ($R^2 = 0.75$). In any matrix other than tissue, this might represent a source (e.g., a factory) that utilized a characteristic mixture of these Aroclors. However, because this fingerprint appears in tissue, it probably represents an aggregate

PCB Congener Study Phase 2 - Source Evaluation

of the various Aroclors used in the LDW, because organisms are exposed to integrated sources as they or the sediment they are exposed to moves within the tidal portion of the river.

Some factors do not resemble Aroclors. In these cases, congeners/peaks that are characteristic of specific sources were identified. For example, PCB-11, PCB-206, PCB-208, and PCB-209 are known to be associated with pigments. Because these pigments are used in a variety of consumer goods, these congeners can enter sewers and storm drains and, therefore, may indicate sources present in treated wastewater, stormwater runoff, or CSO inputs. Thus, some information on the likely identity of these fingerprints is known, but their exact source is somewhat uncertain.

5.0 Conclusions

The results of the analyses described in this source evaluation for each of the five environmental compartments tell a coherent story about PCB contamination in the Green-Duwamish River watershed. The conclusions presented below may be modified in the future as additional PCB congener data become available in environmental media not currently assessed (e.g., groundwater), and/or in locations not represented by the currently available data set.

5.1 General Observations

5.1.1 Aroclor Versus Non-Aroclor Sources

Based on the source evaluation performed as part of this Phase 2 PCB Congener Study, Aroclors are the dominant source of PCBs in the system, with a small contribution from non-Aroclor sources. This conclusion is valid for the places and times for which data are available. As there are limited data available in some environmental compartments, especially surface water in the LDW, this conclusion may not apply generally. To the extent that the data set contains samples representing more than one environmental compartment (e.g., water, sediment, and biota) from a given area, the coherent story extends to the spatial variations of the various Aroclor mixtures. For example, Aroclor 1260 is dominant in the surface water, sediment, and tissue samples near Harbor Island.

Among the Aroclor mixtures, Aroclor 1260 is the dominant PCB source type that was observed, followed by Aroclor 1254, Aroclor 1248, and a small contribution from Aroclors 1242/1016. Because the congener patterns of Aroclors 1242 and 1016 are so similar, no attempt to discriminate between the two has been made.

5.1.2 Microbial Dechlorination

There is no indication of any microbial dechlorination occurring for the locations and times for which data are available. Again, due to the limitations of the data set, there may be pockets of dechlorination that have not been sampled. Previous studies have found that dechlorination of PCBs may occur in river sediments, landfills, groundwater, and sewers, especially combined sewers (Brown et al. 1987; Rodenburg et al. 2010, 2012, 2015a). Groundwater data were not available at the time this study was performed.

The city of Seattle and King County have combined sewers, but the lack of data on surface water in the LDW means that the impact of any dechlorination occurring in these combined sewers would probably not have been visible in the data sets that were examined during this source evaluation. The data from storm drains were collected in the LDW study area and showed no evidence of microbial dechlorination.

One reason microbial dechlorination was not observed, particularly in the East Waterway sediment and water, may be a result of salinity. Microbial dechlorination of PCBs has been shown to be inhibited by sea salt (Abramowicz et al. 1993; Tams and Gradient 1997). However, studies in estuarine systems (Berkaw et al. 1996; Fagerbold et al. 2007; Zanaroli et al. 2012) have shown evidence of microbial dechlorination; therefore, low salinity is not an absolute requirement for the dechlorination process.

5.1.3 Comparison to Other Systems

Dr. Rodenburg's research group has conducted similar source evaluation studies for the New York/New Jersey Harbor (Rodenburg et al. 2011, 2012; Rodenburg and Ralston 2017), the Delaware River (Du et al. 2008; Rodenburg et al. 2010; Praipipat et al. 2013, 2017), and the Portland Harbor Superfund site. The results of these studies are summarized in Figure 5-1. Across all environmental compartments (e.g., air, water, sediment, and permitted discharges) at all of these locations, fingerprints resembling Aroclors were observed, and they were usually the dominant PCB source types.

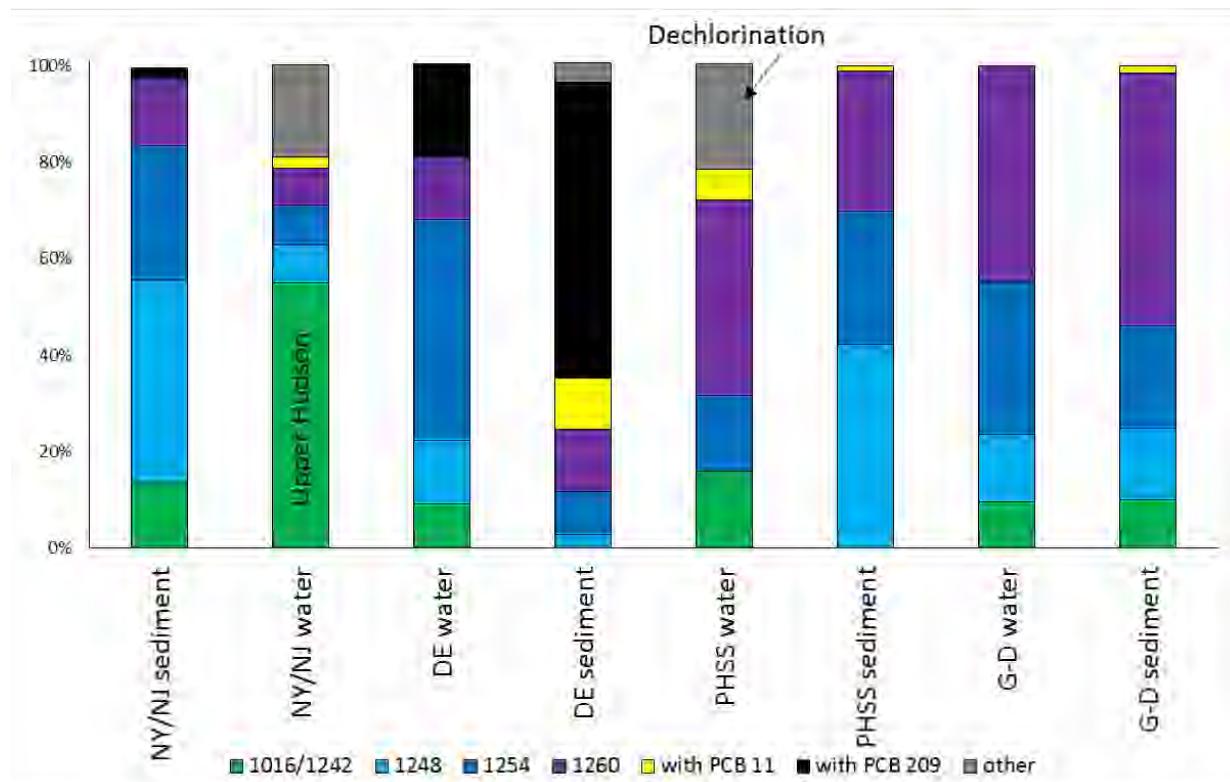


Figure 5-1. PCB Source Types Across Four Watersheds: the New York/New Jersey Harbor (NY/NJ), the Delaware River (DE), the Portland Harbor Superfund Site (PHSS), and the Green-Duwamish Watershed (G-D)

The New York/New Jersey Harbor is an example of a system in which there is one dominant PCB source, namely the Upper Hudson River, where General Electric used primarily Aroclor 1242 (Rodenburg et al. 2011, 2012; Rodenburg and Ralston 2017). The Aroclor 1242 fingerprint was subsequently altered somewhat by microbial dechlorination occurring in the sediment of the Upper Hudson, but the fingerprint is still recognizable as Aroclor 1242. Because this 'weathered' Aroclor 1242 source is relatively low in molecular weight and, therefore, more soluble than other PCB sources, it is proportionately less important as a source to the sediment. The grey 'other' PCB source category in the New York/New Jersey Harbor water represents a fingerprint consisting of Aroclor-type congeners that has been highly weathered and no longer resembles a single Aroclor.

PCB Congener Study Phase 2 - Source Evaluation

The Delaware River is an example of a system in which non-Aroclor sources are much more important (Du et al. 2008; Rodenburg et al. 2010; Praipipat et al. 2013, 2017). A plant in Edgemoor, Delaware, manufactures titanium dioxide via the carbochlorination process that produces titanium tetrachloride, which is subsequently oxidized to titanium dioxide. This process produced significant quantities of PCB-206, PCB-208, and PCB-209. These three congeners represent more than one-half of all the PCB mass in the sediment of the Delaware River. Because these congeners have the highest molecular weights among the PCB congeners, they sorb to sediment and, therefore, represent a larger fraction of the sediment contamination than the water column contamination. The Delaware River also has a significant amount of PCB sediment contamination associated with PCB-11 from organic pigment use in the basin.

The Portland Harbor Superfund site is an example of a system in which extensive microbial dechlorination of PCBs is occurring in the groundwater (Rodenburg et al. 2015a). The seepage of PCBs from groundwater into the river explains the 22 percent of the water column PCB burden that displays a fingerprint indicative of dechlorination. The fact that this fingerprint is not observed in the sediment of the Portland Harbor Superfund site indicates that the dechlorination does not occur in the sediment. The Portland Harbor Superfund site also displays some PCB-11 contamination associated with pigment use in the watershed.

In comparison to these other systems, the Green-Duwamish River system shows less contamination from non-Aroclor PCB sources and no evidence of microbial dechlorination of PCBs. As noted above, these conclusions are only valid for the times and places for which PCB data are available in the Green-Duwamish River system. The Green-Duwamish study area also appears to have more PCB contamination associated with Aroclor 1260 than the other systems.

5.2 Recommendations for Source Control

This study has identified the PCB source types that are most important in the Green-Duwamish River basin, at least for the locations and times for which data are available. This information may be useful for source control activities. Recommendations follow:

- In areas such as storm drains where the PCB sources are expected to resemble specific Aroclors and the concentrations are known or expected to be quite high (i.e., greater than about 2 parts per million), Aroclor methods or even enzyme-linked immunosorbent assay kits may be useful for trackdown. Comparing media concentrations to low regulatory values may still warrant PCB congener analysis.
- The usefulness of this study for source control is limited by the lack of data for some environmental compartments, especially in groundwater and combined sewers. Data from these two compartments could help identify previously unknown sources and might also reveal evidence of microbial dechlorination of PCBs, which can theoretically occur in these two compartments.
- If/when additional data are collected, it may be useful to perform additional PCB source apportionment via PMF. The most important data collection targets are environmental compartments for which there are currently little or no data. As mentioned above, this would include groundwater and combined sewers. Ideally, these new data sets would have at least 60 samples in which most of the targeted 90 peaks were detected to be useful for PMF analysis. For the water column, data are currently very limited in the

LDW, and data collection is planned for this area. Once that data collection is complete or at least 20 to 30 samples have been collected for the LDW, a new round of PMF analysis of the surface water data is warranted.

- Data are currently being collected on PCBs in otter scat. No previous studies in which all 209 PCBs were measured in scat have been identified and, therefore, the congener fingerprints in this scat would be of significant scientific interest.

5.3 Implications for Water Quality Modeling

A chemical fate and transport model (EFDC) of PCBs in the Green-Duwamish River is planned. The results of the initial data assessment and the PMF analysis can provide insights about the best approach for such modeling. There are several issues to consider:

- How much and what kind of PCB data are available?
- What is the end point of modeling (water column concentrations, sediment concentrations, or fish tissue concentrations)?
- What are the budget and time constraints?

5.3.1 How Much and What Kind of Polychlorinated Biphenyl Data are Available?

In general, there are two main approaches that may be used in the PCB EFDC model. PCBs may be modeled as the sum of all congeners (total PCBs) or as homologs. If the homolog approach is adopted, it may not be necessary to model all 10 homologs.

To construct a scientifically defensible homolog model, it must be based primarily on PCB measurements collected using Method 1668. In systems where large numbers of Method 1668 PCB measurements are available, EFDC modeling has often taken the approach of modeling PCB homologs. This is true of the Total Maximum Daily Load model of the Delaware River (Fikslin and Suk 2003), as well as the Contamination Assessment Reduction Project model of the New York/New Jersey Harbor estuary (HydroQual 2007).

In other systems where little or no Method 1668 data are available, PCB EFDC models have focused on total PCBs, or some subset of total PCBs. For example, EFDC models of the Upper Hudson River have modeled total PCBs or Tri+ (PCBs with three or more chlorines) (Connolly et al. 2000; Tams et al. 2000) because most of the data available for the Upper Hudson River come from either Aroclor methods or methods relying on electron capture detection (in the case of the Upper Hudson River, the Green Bay method). Similarly in Green Bay, total PCBs were modeled, as well as five individual congeners (DePinto et al. 1994).

Modeling total PCBs is problematic because the various congeners have very different physicochemical properties, such as octanol-water partition coefficients and Henry's Law constants. The values used for these constants in a total PCB EFDC model would be equivalent to those representing the 'average' PCB molecule, which in the Green-Duwamish River would be a penta- or hexa- PCB. (Note that because the PCB fingerprints vary by location, the 'average' PCB will also vary by location.) The fate of PCBs with properties very different from the average will not be well described by a model of total PCBs. In the Green-Duwamish River system, this is less problematic than in other systems because the mono-, di-, nona-, and deca-

PCB Congener Study Phase 2 - Source Evaluation

homologs (i.e., congeners/homologs with physicochemical properties that are least similar to the average) are not particularly abundant.

Ideally, the data used to generate and calibrate the EFDC model would be measured using the same methods across all samples and compartments and across the geographic area of interest. Two kinds of PCB data are needed: concentrations used to generate PCB loads and boundary conditions, and concentrations used to calibrate the EFDC model. Very little Method 1668 PCB data are available to generate loads and boundary conditions. For calibration, there is a reasonable amount of Method 1668 congener-specific PCB data available for the Green-Duwamish River system, which increases the modeling options. However, because many of those congeners were below detection in the water column, it will be difficult to calibrate an EFDC model for the Green-Duwamish watershed from Method 1668 data alone. In addition, the Method 1668 PCB data (across all five environmental compartments) were collected over a period of many years. For EFDC model calibration, it is preferable that a large volume of high quality data are collected over a short period because running an EFDC model for longer time periods is computationally intensive.

The current plan is to calibrate the EFDC model for the period 1996 through 2007 using existing data. Highest confidence in an EFDC model's ability to explain/predict PCB concentrations is achieved when the model can be shown to accurately reproduce a large body of PCB data from water and sediment (and possibly tissue) across the entire model domain (geographic area) within this model calibration period. This requires large amounts of data, and the more data the better. For these reasons, it might be necessary to use the copious PCB data measured using other methods, including Aroclor methods, to construct loadings or calibrate the EFDC model. Therefore, there are two challenges associated with the present plans for the 1996 through 2007 model calibration period:

- The sum of PCBs calculated from paired samples of Aroclor and Method 1668 data will not agree. A calibration will have to be developed to convert total PCB Aroclors to Method 1668-equivalent total PCBs, and this calibration may be different at various times and places. For example, in the Upper Hudson River, the National Oceanographic and Atmospheric Administration Query Manager (NOAA 2012) contains 23 paired Method 1668/Aroclor samples. In these, the ratio of total PCBs calculated from the Method 1668 data divided by total PCBs calculated from the Aroclor data ranges from 0.3 to 9.3, with an average of 2.8 and a standard deviation of 2.3. There is some evidence that this ratio varies spatially.
- Using the existing data to calibrate the model for the 1996 through 2007 period means that the data used to calibrate the model were not collected at all locations at the same time. Therefore, even a successful model calibration will only demonstrate that the model can accurately predict PCB concentrations in one model sub-region at a time, not simultaneously across the entire EFDC model domain.

The current Green-Duwamish PMF analysis demonstrates that Aroclors 1254 and 1260 are the dominant types of PCBs in this basin. As a result, the tri- through octa- homologs are 'well behaved,' meaning their concentrations are well described by the PMF models. This suggests that modeling those homologs is feasible, and that calibration of such a model should be relatively successful. Modeling mono- or di- homologs will be challenging because they may be susceptible to aerobic degradation, which is difficult to parameterize. In addition, Aroclor and

electron capture detection methods often do a poor job of quantifying the mono- and di-homologs; therefore, calibrating an EFDC model for those homologs can be challenging. This is why the Upper Hudson River models excluded these two homologs in their modeling of Tri+ PCBs.

Both the initial data assessment (Appendix A) and the PMF analysis demonstrate that non-Aroclor sources are not particularly abundant in the Green-Duwamish River basin. Because most of the non-Aroclor congeners fall into homologs mono-, di-, nona-, and deca-, modeling these homologs is likely not necessary at this time.

5.3.2 What is the End Point of Modeling?

In Washington State, relevant regulatory end points exist for the water column, the bed sediments, and target fish tissue. Non-Aroclor congeners, such as PCB-11 (dichloro-), PCB-206 and PCB-208 (nona-), and PCB-209 (deca-), are not particularly abundant in the water and sediment of the Green-Duwamish River basin. This is also true of the fish tissue, because these homologs do not bioaccumulate as efficiently as the medium molecular weight homologs. This further bolsters the conclusion that these homologs are not a priority for EFDC modeling. The dominant homologs in fish tissue are the penta- and hexa- PCBs.

5.3.3 What are the Budget and Time Constraints?

The Green-Duwamish PLA is described as a multi-year and multi-phased project. Data collection and analysis within the watershed have been performed by different entities over time. The EFDC model is being developed based on existing data and with the acknowledgement that additional data are expected from within the LDW as a result of EPA-led pre-remedial design studies associated with the Superfund process. Public funding for additional data collection throughout the watershed is unlikely in the near term. Ecology and EPA, therefore, anticipate maximizing use of currently available data and planned near-term additional data to support the EFDC model calibration and/or simulation period(s). However, the potential for future data collection does exist if such data can be shown to improve usability of the EFDC model.

5.4 Recommendations

For consistency with other watersheds that are updating prior models and for long-term maximum usability, the Green-Duwamish EFDC model should model PCB homologs. Tri-through octa- homologs represent over 99 percent of PCB mass in tissue samples, 98 percent of PCB mass in sediment samples, and 92 percent of PCB mass in water column samples. The most abundant homologs across water, sediment, and biota compartments are the tetra-, penta-, hexa-, and hepta- homologs. These comprise 80 percent of PCB mass in the water column, 87 percent in the sediment, and 91 percent in the biota. These four homologs are the highest priority for modeling.

If the goal is to model PCB homologs, then significant additional data collection will be necessary. This study considers only the additional PCB data to be collected, but other data (e.g., loads of solids and organic carbon) may also be needed.

PCB Congener Study Phase 2 - Source Evaluation

Recommendations for PCB data collection in support of a homolog EFDC model include:

- Gather recommendations from the modeling team on the design of the sampling plan before sampling.
- For best calibration, a new model calibration period could be selected. Targeted intensive data collection could be performed during this period by measuring PCB concentrations (for each homolog or congener that will be simulated), in ideally 100 or more samples of each major environmental medium (e.g., water, sediment, and biota), with emphasis on characterizing the entire range of freshwater discharge and tidal conditions. Ideally, the data that are collected in all environmental media and sources should be from the simulation period of the watershed and receiving water models.
- Use Method 1668 with an SPB-octyl column for all new PCB measurements.
- Measure PCB concentrations for the characterization of loads from point sources (permitted discharges), as well as non-point source(s) (stormwater runoff from non-permitted areas).
- Measure PCB concentrations for characterization of boundary conditions (i.e., in the Salish Sea and in all tributaries to the model domain).
- Measure PCB concentrations at multiple locations within the model domain for calibration.
- Once model calibration is complete, the model can be used to construct simulations decades into the future. As new data become available, they can be used to check the validity of the model predictions and refine the model if necessary.

PCB Congener Study Phase 2 - Source Evaluation

6.0 References

Abramowicz, D.A.; Brennan, M.J.; Van Dort, H.M.; Gallagher, E.L. 1993. "Factors influencing the rate of polychlorinated biphenyls dechlorination in Hudson River sediments." *Environmental Science & Technology* **27**:1125–1131.

Anezaki, K. and Nakano, T. 2014. "Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments." *Environmental Science and Pollution Research* **21**:(2)998–1009.

Ashley, J.T.F.; Secor, D.H.; Zlokovitz, E.; Wales, S.Q.; Baker, J.E. 2000. "Linking habitat use of Hudson River striped bass to accumulation of polychlorinated biphenyl congeners." *Environmental Science & Technology* **34**:1023–1029.

Berkaw, M.; Sowers, K.R.; May, H.D. 1996. "Anaerobic Ortho Dechlorination of Polychlorinated Biphenyls by Estuarine Sediments from Baltimore Harbor." *Appl. Environ. Microbiol.* **62**(7):2534–2539.

Brown, J.F.; Wagner, R.E.; Feng, H.; Bedard, D.L.; Brennan, M.J.; Carnahan, J.C.; May, R.J. 1987. "Environmental dechlorination of PCBs." *Environ. Toxicol. Chem.* **6**:579–593.

Brown, S.G.; Eberly, S.; Paatero, P.; Norris, G.A. 2015. "Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results." *Science of the Total Environment* **518**:626–635.

Buckman, A.H.; Wong, C.S.; Chow, E.A.; Brown, S.B.; Solomon, K.R.; Fisk, A.T. 2006. "Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish." *Aquatic Toxicology* **78**:(2)176–185.

Connolly, J.P.; Zahakos, H.A.; Benaman, J.; Ziegler, C.K.; Rhea, J.R.; Russell, K. 2000. "A model of PCB fate in the upper Hudson River." *Environmental Science & Technology* **34**:4076–4087.

DePinto, J.V.; Raghunathan, R.; Sierzenga, P.; Zhang, X.; Bireman, V.J.; Young, T.C. 1994. *Recalibration of GBTOX: An Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan*.

Du, S.; Belton, T.J.; Rodenburg, L.A. 2008. "Source apportionment of polychlorinated biphenyls in the tidal Delaware River." *Environmental Science & Technology* **42**:4044–4051.

Du, S.; Wall, S.J.; Cacia, D.; Rodenburg, L.A. 2009. "Passive Air Sampling for Polychlorinated Biphenyls in the Philadelphia, USA Metropolitan Area." *Environmental Science & Technology* **43**:1287–1292.

EPA (U.S. Environmental Protection Agency) 1976. *Polychlorinated Biphenyls in the United States, Industrial Use and Environmental Distribution Task I*.

Erickson, M.D. 1997. *Analytical Chemistry of PCBs*. Lewis Publishers.

PCB Congener Study Phase 2 - Source Evaluation

Fagervold, S.K.; May, H.D.; Sowers, K.R. 2007. "Microbial reductive dechlorination of Aroclor 1260 in Baltimore Harbor sediment microcosms is catalyzed by three phylotypes within the Phylum *Chloroflexi*." *Applied and Environmental Microbiology* **73**:3009–3018.

Fikslin, T.J. and Suk, N. 2003. *Total Maximum Daily Loads for Polychlorinated Biphenyls (PCBs) For Zones 2 - 5 Of The Tidal Delaware River*. Report to the U.S. Environmental Protection Agency Regions II and III.

Gamboa, J.A.; Bohe, A.E.; Pasquevich, D.M. 1999. "Carbochlorination of TiO₂." *Thermochim. Acta* **334**:131–139.

Gingrich, S.E. and Diamond, M.L. 2001. "Atmospherically derived organic surface films along an urban-rural gradient." *Environmental Science & Technology* **35**:4031–4037.

Guo, J.; Capozzi, S.L.; Kraeutler, T.M.; Rodenburg, L.A. 2014. "Global Distribution and Local Impacts of Inadvertently Generated Polychlorinated Biphenyls in Pigments." *Environmental Science & Technology* **48**:(15)8573–8580.

Harner, T.; Diamond, M.; Stern, G.; Rosenberg, B. 2004. "Using Passive Air Samplers to Assess Urban-Rural Trends for Persistent Organic Pollutants, Polychlorinated Biphenyls and Organochlorine Pesticides." *Environmental Science & Technology* **38**.

HydroQual 2007. *A Model for the Evaluation and Management of Contaminants of Concern in Water, Sediment, and Biota in the NY/NJ Harbor Estuary. Contaminant Fate, Transport, and Bioaccumulation Sub-models*. Prepared for the Hudson River Foundation on behalf of the Contamination Assessment and Reduction Project (CARP). Available online at: [<http://www.carpweb.org>](http://www.carpweb.org).

Hu, D. and Hornbuckle, K.C. 2010. "Inadvertent Polychlorinated Biphenyls in Commercial Paint Pigments." *Environmental Science & Technology* **44**:2822–2827.

Jansson, S.; Lundin, L.; Grbic, R. 2011. "Characterization and fingerprinting of PCBs in flue gas and ash from waste incineration and in technical mixtures." *Chemosphere* **85**:(3)509–515.

Larsen, R.K. and Baker, J.E. 2003. "Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Models." *Environmental Science & Technology* **37**:1873–1881.

Leidos 2016. *Green-Duwamish River Watershed PCB Congener Study: Phase 1*. Prepared for the Department of Ecology State of Washington Toxics Cleanup Program.

Leidos and Rodenburg (Leidos and L.A. Rodenburg) 2017. *Green-Duwamish River Watershed PCB Congener Study: Phase 2: Initial Data Assessment*. Prepared for the Department of Ecology State of Washington Toxics Cleanup Program.

NOAA (National Oceanographic and Atmospheric Administration). 2012. Query Manager database for the Hudson River, NY. Accessed February 3, 2016. Office of Response and Restoration.

Norris, G.; Wade, K.; Zahn, P.; Brown, S.; Paatero, P.; Eberly, S.; Foley, C. 2009. *Guidance Document for PMF Applications with the Multilinear Engine*. Prepared for the U.S. Environmental Protection Agency.

PCB Congener Study Phase 2 - Source Evaluation

Norris, G.; Duvall, R.; Brown, S.; Bai, S. 2014. *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide*. EPA/600/R-14/108. Prepared for the U.S. Environmental Protection Agency Office of Research and Development.

Paatero, P. and Tapper, U. 1994. "Positive Matrix Factorization: a Non-negative Factor Model with Optimal Utilization of Error Estimates of Data Values." *Environmetrics* **5**:111–126.

Polissar, V.A. and Hopke, P.H. 2001. "Atmospheric Aerosol over Vermont: Chemical Composition and Sources." *Environmental Science & Technology* **35**:4604–4621.

Praipipat, P.; Rodenburg, L.A.; Cavallo, G.J. 2013. "Source Apportionment of Polychlorinated Biphenyls in the Sediments of the Delaware River." *Environmental Science & Technology* **47**:4277–4283.

Praipipat, P.; Meng, Q.; Miskewitz, R.J.; Rodenburg, L.A. 2017. "Source Apportionment of Atmospheric Polychlorinated Biphenyls in New Jersey 1997–2011." *Environmental Science & Technology* **51**:(3)1195–1202.

Reff, A.; Eberly, S.I.; Bhave, P.V. 2007. "Receptor modeling of ambient particulate matter data using positive matrix factorization: Review of existing methods." *Journal of the Air & Waste Management Association* **57**:(2)146–154.

Rodenburg, L.A. 2017. Personal communication between Dr. Lisa Rodenburg (Rutgers University) and Dr. Gary Norris (EPA) regarding PMF 5.0 modeling results.

Rodenburg, L.A. and Meng, Q. 2013. "Source Apportionment of Polychlorinated Biphenyls in Chicago Air from 1996 to 2007." *Environmental Science & Technology* **47**:(8)3774–3780.

Rodenburg, L.A. and Ralston, D.K. 2017. "Historical sources of polychlorinated biphenyls to the sediment of the New York/New Jersey Harbor." *Chemosphere* **169**:450–459.

Rodenburg, L.A.; Guo, J.; Du, S.; Cavallo, G.J. 2009. "Evidence for Unique and Ubiquitous Environmental Sources of 3,3'-Dichlorobiphenyl (PCB 11)." *Environmental Science & Technology* **44**:2816–2821.

Rodenburg, L.A.; Du, S.; Fennell, D.E.; Cavallo, G.J. 2010. "Evidence for Widespread Dechlorination of Polychlorinated Biphenyls in Groundwater, Landfills, and Wastewater Collection Systems." *Environmental Science & Technology* **244**:7534–7540.

Rodenburg, L.A.; Du, S.; Xiao, B.; Fennell, D.E. 2011. "Source Apportionment of Polychlorinated Biphenyls in the New York/New Jersey Harbor." *Chemosphere* **83**:792–798.

Rodenburg, L.A.; Du, S.Y.; Lui, H.; Guo, J.; Oseagulu, N.; Fennell, D.E. 2012. "Evidence for Dechlorination of Polychlorinated Biphenyls and Polychlorinated Dibenzo-p-Dioxins and -Furans in Wastewater Collection Systems in the New York Metropolitan Area." *Environmental Science & Technology* **46**(12):6612–6620.

Rodenburg, L.A.; Krumins, V.; Curran, J.C. 2015a. "Microbial Dechlorination of Polychlorinated Biphenyls, Dibenzo-p-dioxins, and -furans at the Portland Harbor Superfund Site, Oregon, USA." *Environmental Science & Technology* **49**(12):7227–7235.

PCB Congener Study Phase 2 - Source Evaluation

Rodenburg, L.A.; Delistraty, D.; Meng, Q. 2015b. "Polychlorinated Biphenyl Congener Patterns in Fish near the Hanford Site (Washington State, USA)." *Environmental Science & Technology* **49**(5):2767–2775.

Rodenburg, L.A.; Guo, J.; Christie, R. 2015c. "Polychlorinated biphenyls in pigments: inadvertent production and environmental significance." *Coloration Technology* **131**:353–369.

Rushneck, D.R.; Beliveau, A.; Fowler, B.; Hamilton, C.; Hoover, D.; Kaye, K.; Berg, M.; Smith, T.; Telliard, W.A.; Roman, H.; Ruder, E.; Ryan, L. 2004. "Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA Method 1668A." *Chemosphere* **54**:79–87.

Tams and Gradient (Tams Consultants and Gradient Corporation) 1997. *Phase 2 Report - Further Site Characterization and Analysis Volume 2C - Data Evaluation and Interpretation Report Hudson River PCBs Reassessment RI/FS*. Prepared for the U.S. Environmental Protection Agency and U.S. Army Corps of Engineers.

Tams, Limno-Tech, Menzie-Cura and Associates, and Tetra Tech (Tams Consultants; Limno-Tech, Inc.; Menzie-Cura and Associates; and Tetra Tech) 2000. *Phase 2 Report, Further Site Characterization and Analysis, Volume 2D - Revised Baseline Modeling Report Hudson River Polychlorinated Biphenyls Reassessment Remedial Investigation/Feasibility Study*. Prepared for the U.S. Environmental Protection Agency Region 2 and U.S. Army Corps of Engineers.

Zanaroli, G.; Ballo, A.; Negroni, A.; Borruso, L.; Daffonchio, D.; Fava, F. 2012. "A *Chloroflexi* bacterium dechlorinates polychlorinated biphenyls in marine sediments under in situ-like biogeochemical conditions." *J. Hazard. Mater.* Netherlands, A 2012 Elsevier B.F. **209-210**:449–457.

Appendix A
Initial Data Assessment Memorandum

PCB Congener Study Phase 2 - Source Evaluation

Green-Duwamish River Watershed

PCB Congener Study: Phase 2 Initial Data Assessment

Prepared for



Toxics Cleanup Program
Northwest Regional Office
Washington State Department of Ecology
Bellevue, Washington

Prepared by

Dr. Lisa A. Rodenburg

and



Leidos
18912 North Creek Parkway, Suite 101
Bothell, Washington 98011

January 2017

Limitation of Use: Leidos' project activities were restricted to analysis of records made available by the Washington State Department of Ecology (Ecology) or third parties during the project. In preparing this report, Leidos has relied on verbal and written information provided by secondary sources and interviews, including information provided by the customer. Leidos has made no independent investigations concerning the accuracy or completeness of the information relied upon. Because the project activities consisted of evaluating a limited supply of information, Leidos may not have identified all potential items of concern and, therefore, Leidos warrants only that the project activities under this contract have been performed within the parameters and scope communicated by Ecology and reflected in the contract. Maps presented in this report were accurate based on the information available to Leidos.

This report is intended to be used in its entirety. Taking or using in any way excerpts from this report is not permitted, and any party doing so does so at its own risk.

Table of Contents

	<u>Page</u>
1.0 Introduction.....	1
1.1 Measurement of Polychlorinated Biphenyls.....	2
1.2 Quality Control	3
2.0 General Features of the Data Set.....	8
2.1 Gas Chromatography Columns.....	12
2.2 Blanks	14
2.3 Surrogate Recoveries	14
3.0 Air Deposition Data	15
3.1 Data Summary	15
3.2 Blanks	15
3.3 Obvious Patterns	15
3.4 Suitability for Factor Analysis	16
4.0 Surface Water Data	17
4.1 Data Summary	17
4.2 Blanks	17
4.3 Obvious Patterns	19
4.4 Suitability for Factor Analysis	19
5.0 Sediment Data	20
5.1 Data Summary	20
5.2 Blanks	20
5.3 Obvious Patterns	20
5.4 Suitability for Factor Analysis	20
6.0 Storm Drain Data.....	21
6.1 Data summary	21
6.2 Blanks	21
6.3 Obvious Patterns	21
6.4 Suitability for Factor Analysis	21
7.0 Tissue Data	22
7.1 Data Summary	22
7.2 Blanks	22
7.3 Obvious Patterns	22
7.4 Suitability for Factor Analysis	22
8.0 Conclusions and Proposed Methodology	23
8.1 Treatment of Non-Detects.....	23
9.0 Recommendations for Data Collection and Management Improvements.....	25
10.0 References.....	26

*PCB Congener Study Phase 2 – Initial Data Assessment***Tables**

	<u>Page</u>
Table 1. PCB Congener Coelution Patterns on the SPB-octyl and DB-5 (or equivalent) GC Columns	4
Table 2. Studies Selected for Inclusion in the Phase 2 Study	9
Table 3. Summary of Samples Available from Each Study in Each Medium.....	13
Table 4. Congeners/Peaks that are Most Closely Correlated with PCB-68 in Water Samples from Studies 14 and 15	18
Table 5. Number of Samples Available for Factor Analysis by Medium and the Percent of Data Points that will be Below Detection Limits in the Input Matrix.....	23

Acronyms and Abbreviations

COC	chemical of concern
CSO	combined sewer overflow
DRBC	Delaware River Basin Commission
Ecology	Washington State Department of Ecology
EDD	electronic data deliverable
EIM	Environmental Information Management System
EPA	U.S. Environmental Protection Agency
FS	Feasibility Study
GC	gas chromatography
LDW	Lower Duwamish Waterway
MS	mass spectrometer
ng/m ² /day	nanograms per square meter per day
NPDES	National Pollutant Discharge Elimination System
PCA	principle components analysis
PCB	polychlorinated biphenyl
pg/L	picograms per liter
PMF	positive matrix factorization
PSAMP	Puget Sound Assessment and Monitoring Program
QA	quality assurance
QC	quality control
RI	Remedial Investigation
RT	retention time
STORET	STOrage and RETrieval (an electronic data system for water quality monitoring data developed by EPA)
TEF	toxic equivalency factor
TEQ	toxic equivalency quotient

PCB Congener Study Phase 2 – Initial Data Assessment

1.0 Introduction

The *Green-Duwamish River Watershed PCB Congener Study: Phase 1 Report* (Leidos 2016a) describes how thousands of environmental samples have been collected in the Green-Duwamish River Watershed, and particularly in the Lower Duwamish Waterway (LDW), over the past 30 years. Sampled media include surface and subsurface river sediments, soil, groundwater, surface water, stormwater, storm drain solids, building materials, fish and shellfish tissue, and air. Many of these samples have been analyzed for polychlorinated biphenyls (PCBs), primarily as Aroclors. In recent years, some environmental samples have been analyzed for PCB congeners; congener analysis provides lower detection limits and is potentially more useful in identifying sources of PCB contamination (Leidos 2016a). The objective of the Green-Duwamish River Watershed PCB Congener Study: Phase 2 is to identify the types of sources that are contributing to PCB pollution in the Green-Duwamish River and the LDW. The first step, described in this Phase 2 Initial Data Assessment Report, is to evaluate the existing congener-specific PCB data to determine whether it can be used for the source apportionment modeling step of the evaluation.

The proposed source evaluation technique consists of performing positive matrix factorization (PMF) using the concentrations of PCB congeners in the selected samples. The samples would be grouped by media into air, water, sediment, and biological tissue. PMF is an advanced factor analysis method developed by Paatero and Tapper (1994), and it has two main advantages over simpler techniques, such as principle components analysis (PCA). First, in PMF, error estimates for individual values are used to weight the data. The inclusion of uncertainties provides a means for including species with missing values and data below detection limits; highly uncertain measurements are down-weighted and have less influence on the solution. Second, a non-negativity constraint is imposed on the PMF solution. As a result, the PMF solution resembles a chemical mass balance model, in which the PMF program attempts to account for all of the mass of the analytes in each sample. This represents another major advantage of the PMF model over PCA, which often generates negative source contributions (Larsen and Baker 2003).

The congener-specific PCB data included in this assessment have previously undergone extensive quality assurance (QA) and quality control (QC) evaluation, and the vast majority have been deemed to meet the QA/QC criteria. To conduct a useful PMF analysis, the data must meet some additional criteria:

- There must be enough data; at least as many samples as there are congeners (peaks).
- Most of the concentrations must be above the detection limit. Too many data that are below the detection limit can prevent the PMF model from finding a solution, or cause it to produce a solution that is not useful...
- In the PMF model, each data point is assigned an uncertainty, which is determined by previously identified information regarding surrogate recoveries (explained below). When surrogate recovery data are not available, information regarding reproducibility, obtained by analyzing the same sample more than once (i.e., duplicates), can be used.
- It is helpful, but not necessary, to know the detection limits for each congener/peak in each sample.

PCB Congener Study Phase 2 – Initial Data Assessment

Therefore, this Phase 2 Initial Data Assessment Report determines the amount of congener-specific PCB data that are of sufficient quality that it can be used in a PMF analysis to determine the sources of pollution in the Duwamish-Green River Watershed.

1.1 Measurement of Polychlorinated Biphenyls

The congener-specific PCB data evaluated here were collected using U.S. Environmental Protection Agency (EPA) Method 1668, which was first published in 1999 and has undergone several revisions since then (EPA 1999). The first version was Method 1668A, and subsequent minor revisions are denoted as 1668B, 1668C, and 1668D. There is relatively little difference between the various revisions, and data collected under different revisions are highly comparable and can generally be pooled and used together. For simplicity, this Phase 2 Initial Data Assessment Report refers to Method 1668 without specifying a revision number. Method 1668 uses a high-resolution mass spectrometer (MS) coupled with high-resolution gas chromatography (GC) to measure PCBs in any matrix. Chromatography is the science of separating a mixture into its individual components by injecting the mixture into a mobile phase, which then passes through a stationary phase. Some compounds in the mixture spend more time sorbed onto the stationary phase. Because these compounds spend more time not moving, they will emerge (elute) from the chromatographic system later. The amount of time a compound takes to travel through the chromatographic system is its retention time. In GC, the mobile phase is a gas (usually helium), and the stationary phase can be any one of a number of organic compounds chemically bonded to a stationary support. There are hundreds of GC columns commercially available. The primary mechanism causing some PCB congeners to be retained longer on any of these columns is their condensation on the stationary phase; therefore, the primary chemical property that determines the retention time is the compound's vapor pressure. The type of stationary phase has a lesser, but still important, impact on the compound's retention time.

There are 209 PCB congeners. A homolog group is a set of congeners that have the same number of chlorines. The MS used in Method 1668 can discern between different masses of the PCB molecule; therefore, congeners that have the same retention time but different masses (i.e., different homologs) can be quantified separately. The key difficulty in measuring PCBs is that, within a homolog group, there are often several congeners that are so similar in their vapor pressure, that they have essentially the same retention time; therefore, they cannot be quantified separately and can only be reported as the sum of multiple congeners. One of the primary goals when developing Method 1668 was to find a column that would resolve the 12 dioxin-like PCB congeners into 12 separate peaks, each with its own unique retention time, such that none of the 12 coelute with any other PCB congener. This would allow the results to be used to calculate a toxic equivalency quotient (TEQ) by multiplying the concentration of each dioxin-like congener by its corresponding toxic equivalency factor (TEF).

Separating the 12 dioxin-like congeners from all the others is difficult. Even after much effort, Method 1668 could only separate 10 of the 12 completely, with the 2 remaining dioxin-like congeners (PCB-156 and PCB-157) coeluting with each other using an SPB-octyl column. Fortunately, PCB-156 and PCB-157 have the same TEF; therefore, the calculation of the TEQ was not affected. However, the column that had been most commonly used for PCB analysis since the 1980s *could* separate PCB-156 and PCB-157 into 2 separate peaks, but it could not resolve all of the other 10 dioxin-like congeners. This column is referred to as DB-1 in

PCB Congener Study Phase 2 – Initial Data Assessment

Method 1668, but it is also referred to as DB-5, as well as a number of other names. (Throughout this Phase 2 Initial Data Assessment Report, DB-5 is used to refer to any GC column equivalent to DB-5.¹) The authors of Method 1668 allowed this column as an alternate. As written, Method 1668 requires the use of “[a]ny GC column or column system (2 or more columns) that provides unique resolution and identification of the Toxics for determination of a TEQ_{PCB} using TEFs...Isomers may be unresolved so long as they have the same TEF and response factor and so long as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-octyl column...achieves unique GC resolution of all Toxics except congeners with IUPAC numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor... The DB-1 column is optional and is capable of uniquely resolving the congener pair with IUPAC 156 and 157” (EPA 1999).

To complicate matters further, recently SGE Analytical Science developed a column called the SGE-HT8, which is capable of resolving more congeners than the DB-5 and is more rugged than the SPB-octyl. This column is now sometimes used for PCB analysis by Method 1668.

As noted, there is no column that can separate all 209 congeners into 209 separate peaks. Some congeners will always coelute. The problem is that the coelution patterns are very different on the SPB-octyl, SGE-HT8, and DB-5 equivalent columns. Table 1 summarizes the most common coelution patterns, but small differences can be observed depending on the lot and age of the GC column. This has led to much confusion.

Contract laboratories are, technically, allowed to use any of these columns. Unless the customer specifies a specific column, they cannot know what kind of data they will be given. As Table 1 demonstrates, if the goal is to mix data collected on the different types of columns into a single data set for analysis, many concentrations reported for a variety of congeners must be summed. One example is PCB-85. On the DB-5 column, six separate reported concentrations must be summed to equal the sum of three reported concentrations from the SPB-octyl column, which yields a single concentration representing the sum of PCB congeners 85, 86, 87, 97, 108, 112, 116, 117, 119, and 125. Information is lost. As a result, while the DB-5 column reports the 209 PCBs in 168 chromatographic peaks, and the SPB-octyl column reports the 209 congeners in 159 peaks, a data set in which SPB-octyl and DB-5 data have been combined will contain only 128 peaks. A data set in which all three types of columns have been used will contain only 122 peaks after they are composited.

1.2 Quality Control

Measuring low concentrations of organic pollutants in complex environmental samples is both challenging and expensive. Therefore, it is extremely important to conduct a number of tests to ensure that the data are of high quality. Method 1668 contains some important QC measures, one of which is the use of surrogate compounds to measure the efficiency of the measurement process. In Method 1668, samples are first extracted (i.e., they are exposed to an organic solvent

¹ Columns equivalent to the DB-5 include Rtx-5, Rtx-5MS, Rxi-5HT, DB-5ht, DB-5MS, HP-5, HP5-MS, ZB-5, OPTIMA 5, OPTIMA 5-MS, SPB-5, and many others. See <http://www.restek.com/Chromatography-Columns/GC-Columns/GC-Column-Cross-Reference-Columns-by-Phase> for a more complete list. Note that the SGE-HT8 which is also sometimes used in PCB congener analysis is similar to, but not the same as, the DB-5.

*PCB Congener Study Phase 2 – Initial Data Assessment***Table 1. PCB Congener Coelution Patterns on the DB-5 (or equivalent), SGE-HT8, and SPB-octyl GC Columns**

DB-5	SGE-HT8	SPB-octyl	Matched Pattern
PCB-4+10	PCB-4 PCB-10	PCB-4 PCB-10	PCB-4+10
PCB-5+8	PCB-5+8	PCB-5 PCB-8	PCB-5+8
PCB-7+9	PCB-7 PCB-9	PCB-7 PCB-9	PCB-7+9
PCB-12+13	PCB-12+13	PCB-12+13	PCB-12+13
PCB-16+32	PCB-16 PCB-32	PCB-16 PCB-32	PCB-16+32
PCB-18 PCB-30	PCB-18 PCB-30	PCB-18+30	PCB-18+30
PCB-20+21+33 PCB-28	PCB-20+33 PCB-21 PCB-28	PCB-20+28 PCB-21+33	PCB-20+21+28+33
PCB-24+27	PCB-24 PCB-27	PCB-24 PCB-27	PCB-24+27
PCB-26 PCB-29	PCB-26 PCB-29	PCB-26+29	PCB-26+29
PCB-40 PCB-41+64+71+72 PCB-57	PCB-40+57 PCB-41 PCB-64+72 PCB-71	PCB-40+41+71 PCB-57 PCB-64 PCB-72	PCB-40+41+57+64+71+72
PCB-42+59 PCB-43+49 PCB-44 PCB-47 PCB-48+75 PCB-52+69 PCB-62 PCB-65	PCB-42 PCB-43+49 PCB-44 PCB-47+48 PCB-52+69 PCB-49 PCB-62 PCB-65+75	PCB-42 PCB-43 PCB-44+47+65 PCB-48 PCB-49+69 PCB-52 PCB-59+62+75	PCB-42+43+44+47+48+49+ 52+59+62+65+69+75
PCB-45 PCB-51	PCB-45 PCB-51	PCB-45+51	PCB-45+51
PCB-50 PCB-53	PCB-50 PCB-53	PCB-50+53	PCB-50+53
PCB-56+60	PCB-56 PCB-60	PCB-56 PCB-60	PCB-56+60

PCB Congener Study Phase 2 – Initial Data Assessment

DB-5	SGE-HT8	SPB-octyl	Matched Pattern
PCB-61+70 PCB-66+76 PCB-74	PCB-61 PCB-66 PCB-70 PCB-74 PCB-76	PCB-61+70+74+76 PCB-66	PCB-61+66+70+74+76
PCB-83 PCB-85+116 PCB-86 PCB-87+117+125 PCB-97 PCB-99 PCB-107+109 PCB-108+112 PCB-110 PCB-111+115 PCB-119 PCB-124	PCB-83+109 PCB-85 PCB-86+97+117 PCB-87+115 PCB-99 PCB-107+108 PCB-110 PCB-111 PCB-112+119 PCB-116+125 PCB-124	PCB-83+99 PCB-85+116+117 PCB-86+87+97+108+119 +125 PCB-107+124 PCB-109 PCB-110+115 PCB-111 PCB-112	PCB-83+85+86+87+97+99+ 107+108+109+110+111+112+ 115+116+117+119+124+125
PCB-84+92	PCB-84 PCB-92	PCB-84 PCB-92	PCB-84+92
PCB-88+91	PCB-88 PCB-91	PCB-88+91	PCB-88+91
PCB-93 PCB-95+98+102 PCB-100	PCB-93+98+102 PCB-95 PCB-100	PCB-93+95+98+100+102	PCB-93+95+98+100+102
PCB-90+101 PCB-113	PCB-90 PCB-101 PCB-113	PCB-90+101+113	PCB-90+101+113
PCB-105 PCB-127	PCB-105+127	PCB-105 PCB-127	PCB-105+127
PCB-106+118	PCB-106 PCB-118	PCB-106 PCB-118	PCB-106+118
PCB-128+162 PCB-166	PCB-128 PCB-162 PCB-166	PCB-128+166 PCB-162	PCB-128+162+166
PCB-129 PCB-138+163+164 PCB-158+160	PCB-129 PCB-138 PCB-158 PCB-160 PCB-163+164	PCB-129+138+160+163 PCB-158 PCB-164	PCB-129+138+158+160+163+164
PCB-132+161	PCB-132+161	PCB-132 PCB-161	PCB-132+161

PCB Congener Study Phase 2 – Initial Data Assessment

DB-5	SGE-HT8	SPB-octyl	Matched Pattern
PCB-133+142	PCB-133 PCB-142	PCB-133 PCB-142	PCB-133+142
PCB-135 PCB-151 PCB-154	PCB-135 PCB-151 PCB-154	PCB-135+151+154	PCB-135+151+154
PCB-136 PCB-148	PCB-136+148	PCB-136 PCB-148	PCB-136+148
PCB-134+143 PCB-139+149 PCB-140 PCB-146+165 PCB-147	PCB-134 PCB-139+149 PCB-140 PCB-143 PCB-146 PCB-147 PCB-165	PCB-134+143 PCB -139+140 PCB-146 PCB-147+149 PCB-165	PCB-134+139+140+143+146+147+ 149+165
PCB-153 PCB-168	PCB-153 PCB-168	PCB-153+168	PCB-153+168
PCB-156 PCB-157	PCB-156 PCB-157	PCB-156+157	PCB-156+157
PCB-171 PCB-173	PCB-171 PCB-173	PCB-171+173	PCB-171+173
PCB-180 PCB-193	PCB-180 PCB-193	PCB-180+193	PCB-180+193
PCB-182+187	PCB-182+187	PCB-182 PCB-187	PCB-182+187
PCB-183 PCB-185	PCB-183 PCB-185	PCB-183+185	PCB-183+185
PCB-196+203	PCB-196 PCB-203	PCB-196 PCB-203	PCB-196+203
PCB-197 PCB-200	PCB-197 PCB-200	PCB-197+200	PCB-197+200
PCB-198 PCB-199	PCB-198 PCB-199	PCB-198+199	PCB-198+199

Congeners that do not coelute on any column are not shown.

GC = Gas chromatography.

PCB = Polychlorinated biphenyl.

PCB Congener Study Phase 2 – Initial Data Assessment

into which the organic chemicals, such as PCBs, dissolve). Next, the volume of the sample is reduced by evaporating away the excess solvent. The concentrated sample is then cleaned up (i.e., interfering compounds are removed) via one or more methods, including passing the sample through a column containing silica gel. The sample is then reduced in volume once more and then analyzed by GC using a high-resolution MS.

Because of the many steps involved, some amount of the target analyte could be lost. The surrogate compounds are designed to measure this amount. Method 1668 allows more than 30 surrogate congeners. These are PCB congeners in which the normal carbon with an atomic weight of 12 has been replaced with a carbon isotope with an atomic weight of 13 (termed ^{13}C). Because this substitution changes the mass of the molecule, the MS can measure the regular PCB and the ^{13}C -labeled PCB separately, even though they have exactly the same retention time. These ^{13}C -labeled congeners are added at various stages of sample collection and handling, and the amount quantified at the end of the process relative to the amount added is referred to as the surrogate recovery. The ideal surrogate recovery is 100 percent (i.e., 100 percent of the surrogate added to the sample is extracted and measured), but Method 1668 specifies that recoveries between 25 and 150 percent are acceptable (30 to 135 percent for cleanup surrogates, which are injected just prior to the cleanup step). Contract laboratories do not typically report surrogate recoveries, but they can, if asked.

Another important QA practice is the analysis of blanks. There are several possible types of blanks, including field blanks (e.g., sampling media handled in the field and transported along with samples), laboratory method blanks (e.g., sampling media generated in the laboratory and analyzed along with samples), and rinsate blanks (e.g., ‘clean’ water collected after it has been used to rinse the sample collection apparatus). In this Phase 2 Initial Data Assessment, different types of blanks are treated as though they are equivalent. Because PCBs are ubiquitous, keeping blanks clean is challenging. Even under ideal circumstances, PCBs will be detected in blanks, and the study leader must determine how to handle any blank contamination. Blank issues are most often a problem for water samples. For example, in Study 13 (see Section 2.0), 10 blanks had an average concentration of total PCB congeners of approximately 37 picograms per liter (pg/L), while the average concentration in the water samples was approximately 700 pg/L, thus suggesting that blank contamination could account for approximately 5 percent of the PCBs measured in the samples.

Contract laboratories strive to achieve the lowest possible detection limits, so that as many PCB peaks as possible can be quantified. The detection limit depends on several factors, including the sensitivity of the instrument, the size of the sample (e.g., volume of water or mass of sediment or tissue), and the concentrations of PCBs in the blanks. Limits of detection should be reported even when the analyte is detected, so that the user of the data can evaluate the signal-to-noise ratio². The greatest confidence in detected PCB peaks exists when they are many times larger than the background noise. Very small peaks are detectable and reported as concentrations, but there is less confidence that their reported values are precise and/or accurate.

² Signal-to-noise ratio is defined as the ratio of the level of a desired signal to the level of background noise.

2.0 General Features of the Data Set

Under Phase I of this study (Leidos 2016a), Leidos compiled a draft database of available PCB congener data in the Green-Duwamish Watershed. As part of the current Phase 2, the database structure was modified, new data were added, a quality assurance/quality control (QA/QC) review was performed, and errors were corrected. Additional reviews, corrections, and additions are in progress, in response to issues identified during the data assessment described in this report. The current dataset include over 1,500 samples analyzed for a subset or full suite of PCB congeners in various media, including sediment, tissue, surface water, storm drain solids, stormwater, and air deposition samples. No groundwater samples and only three soil samples (plus field replicates) with PCB congener analysis were identified. Approximately 700 samples from 225 locations in the Green-Duwamish River watershed were analyzed for the full suite of PCB congeners. The full-suite congener data were selected for further consideration during this Phase 2 initial data assessment.

The current working database for PCB congeners in the Green-Duwamish River watershed is a Microsoft Access® database ('database') comprised of the following five tables³:

- (1) Study – includes the study name and purpose; the range of sampling dates; contact information; submitting organization; and study QA planning level.
- (2) Location – includes the study location names and settings; addresses; source control area if in the LDW; and latitude/longitude.
- (3) Sample – includes the sample matrix; PCB analysis type (e.g., full suite congeners, Aroclors, etc.); sample date; sample depth (if from a core); whether the sample is a replicate and, if so, what type (laboratory, field, etc.); and the tissue type and species if a tissue sample.
- (4) Results – includes the results for each parameter measured, data qualifiers, detection limits, reporting limits, sample fraction, and basis (wet or dry).
- (5) Laboratory QA – includes the name of the laboratory where the analysis was conducted, the sample preparation method, and the analysis method and date.

Studies that include full-suite PCB congener data were considered for inclusion in the Phase 2 PCB source evaluation. These studies are described in Table 2.

³ Many of the fields in the database are intended for future use and are not currently populated. Limited information was available for the historical studies included in the current working database.

*PCB Congener Study Phase 2 – Initial Data Assessment***Table 2. Studies Considered for Inclusion in the PCB Source Evaluation**

Study Code	Study Name	Medium¹	Location Type	Description
2	LDW Site, Boeing Split Samples (2006, 2009)	Soil, Other Solids	Upland	Study performed to support litigation between the City of Seattle and Boeing, including three soil sampling locations (sampled in May 2006) and five samples of surface debris, sampled in July 2009.
5	LDW, East Waterway and West Waterway Subsurface Sediment (2012)	Sediment	Receiving Water	Study to determine the level of contamination in subsurface sediments of the LDW, East Waterway, and West Waterway; compare analytical techniques for PCB analysis; and monitor the Confined Aquatic Disposal site in the West Waterway. Samples were collected in 2012, and a subset was analyzed for the full suite of PCB congeners.
6	East Waterway Supplemental RI/FS	Surface Water, Sediment, Tissue	Receiving Water	Water, sediment, and tissue sampling in support of the East Waterway RI/FS. Tissue samples include fish and shellfish.
9	LDW RI - Fish and Crab (2004)	Tissue	Receiving Water	An investigation of the nature and extent of contamination to support ecological and human health risk assessment. Six species of fish (English sole, starry flounder, Pacific staghorn sculpin, pile perch, shiner perch, and striped sea perch) and two species of crab (Dungeness and slender) were collected in August and September 2004.
12	Green River Loading Study - Phase 1 (2013)	Surface Water, Sediment, Suspended Solids	Receiving Water	A study to assess sediment and chemical loading from the Green River to the LDW. Samples were collected between February and June 2013. A subset of samples was analyzed for the full suite of PCB congeners.
13	Green River Loading Study - Phase 2 (2014-2015)	Surface Water, Sediment, Suspended Solids	Receiving Water	A follow-on study to assess sediment and chemical loading from the Green River to the LDW. Sediment, water, and suspended solids samples were collected between January 2014 and March 2015.
14	King County Green River Watershed Surface Water (2011-2012)	Surface Water	Receiving Water	Study to assess the relative contribution of COCs to the LDW from upstream areas in the Green River. Surface water samples were collected in 2011 and 2012 from four major tributaries to the Green River, as well as at two locations on the main stem of the Green River.
15	King County Upper and Middle Green River Surface Water (2013-2014)	Surface Water	Receiving Water	Study to assess the relative concentrations of key LDW COCs in the upper and middle reaches of the Green River. Samples were collected in 2013 and 2014 from two sites above the Howard Hanson Dam and from one below.
16	King County LDW Bulk Atmospheric Deposition Study (2011-2012)	Air Deposition	Upland	Study to evaluate the atmospheric deposition of pollutants (bulk deposition of dry particulates and precipitation) in the Green-Duwamish River Basin. Samples were collected at five stations in 2011 and 2012, with a sixth station added toward the end of the study.

*PCB Congener Study Phase 2 – Initial Data Assessment***Table 2. Studies Considered for Inclusion in the PCB Source Evaluation (continued)**

Study Code	Study Name	Medium¹	Location Type	Description
17	PSAMP Groundfish Contaminant Survey – PCB Reanalysis (2007)	Tissue	Receiving Water	As part of the LDW RI, the Lower Duwamish Waterway Group reanalyzed six English sole tissue samples in May 2007 (from a single location) for Aroclors and the full suite of PCB congeners.
18	LDW RI - Fish Collection (2005)	Tissue	Receiving Water	An investigation of PCB concentrations in fish in the LDW. English sole and shiner perch were collected in August and September 2005.
19	Fish, Crab, and Clam Tissue Collection and Chemical Analyses in the LDW (2007)	Tissue	Receiving Water	Study to provide additional insight into PCB concentrations in tissue of six aquatic species found in the LDW. Congener analyses included slender crab, Dungeness crab, shiner perch, and English sole.
20	NPDES Inspection Sampling Support (2013)	Storm Drain Water	Upland	Study to investigate the presence of contaminants in stormwater and storm drain solids at NPDES-permitted facilities discharging to the LDW. Only the water samples collected in this study were analyzed for the full suite of PCB congeners.
21	NPDES Inspection Sampling Support (2014-2015)	Storm Drain Water/Solids	Upland	Continuation of Study 21. All water and solids samples collected in 2014 and 2015 were analyzed for the full suite of PCB congeners.
22	S 96 th Street/Hamm Creek Sediment Trap and Stream Sampling (2015)	Surface Water, Sediment, Storm Drain Water/Solids,	Receiving Water and Upland	Study to characterize the water, sediment, and storm drain solids in the S 96th Street storm drain and Hamm Creek drainage subbasins. All samples were analyzed for the full suite of PCB congeners.
23	King County Water Sampling (2005-2008)	Surface Water	Receiving Water	Four locations were sampled between 2005 and 2008. Samples were collected at 1 meter above the river bottom and 1 meter below the water surface. All samples were analyzed for the full suite of PCB congeners.
26	LDW RI Clams and Benthic Invertebrates (2004)	Tissue	Receiving Water	An investigation of the nature and extent of contamination to support ecological and human health risk assessment. Soft-shell clams and amphipods were collected in 2004. Co-located surface sediment samples were analyzed for a subset of PCB congeners only. ²

*PCB Congener Study Phase 2 – Initial Data Assessment***Table 2. Studies Considered for Inclusion in the PCB Source Evaluation (continued)**

Study Number	Study Name	Medium¹	Location Type	Description
27	LDW Upstream Sediment Analysis (2008)	Sediment	Receiving Water	Re-analysis of a subset of surface sediment samples collected by Ecology in 2008 in support of Ecology's contaminant loading study for the LDW.
38	King County CSO Sampling (2007-2010)	Combined Sewer Water	Upland	Study included collection of samples that represent CSOs in the Duwamish River Basin. Samples were collected at partially to near-full conditions of the combined sewers at seven locations, four in the LDW and three in the East Waterway. All samples were analyzed for the full suite of PCB congeners.
39	King County LDW Supplemental Bulk Atmospheric Deposition Study (2013)	Air Deposition	Upland	Study supplements the 2011/2012 Bulk Atmospheric Deposition Study (Study 16). It was designed to increase the ability to detect temporal trends and relationships with weather parameters and air concentrations of fine particulate matter.
40	King County Green River Watershed Suspended Solids (2016 Draft)	Suspended Solids	Receiving Water	Assessment of chemical concentrations in suspended solids in the Green River Watershed, as presented in a 2016 draft report. Samples were collected from two locations in and four major tributaries to the Green River using two sampling methods: sediment traps and filtered solids.

¹ Media include only those analyzed for full suite PCB congeners; media analyzed for congener subsets and/or Aroclors are not included.

² The Phase I data report incorrectly stated that this study included full suite congener analysis of the surface sediment samples, but full suite congeners were only analyzed for the tissue samples from this study.

Ecology = Washington State Department of Ecology.

COC = Chemical of concern.

CSO = Combined sewer overflow.

FS = Feasibility study.

LDW = Lower Duwamish Waterway.

NPDES = National Pollutant Discharge Elimination System.

PCB = Polychlorinated biphenyl.

PSAMP = Puget Sound Assessment and Monitoring Program.

RI = Remedial investigation.

Table 3 summarizes the number of samples and other information about the studies included with each medium. In general, the data quality is good, and most of it is suitable for factor analysis. This Phase 2 Initial Data Assessment examined the congener-specific Method 1668 PCB data only and did not examine other ancillary data that might impact the usefulness of the PCB data, such as sampling locations and measurements of variables, such as total organic carbon and particulate organic carbon.

A thorough examination of the Method 1668 PCB data has been conducted. The PCB Congener Study, Phase 1 Report (Leidos 2016a) identified Method 1668 PCB data in the following environmental media: sediment, tissue, surface water, suspended solids, storm drain solids,

storm drain water, combined sewer water, air deposition, soil, and other upland solids. After reviewing the available data, it is recommended the media be combined, as shown below, to provide a sufficient number of sample data to perform factor analysis:

- Air,
- Surface water,
- Sediment (including suspended solids),
- Storm drains (water and solids), and
- Tissue (biota).

There are not sufficient soil samples analyzed for PCB congeners to run factor analysis, therefore Study 2 will not be considered further. Based on Ecology input, combined sewer water samples (Study 38) are considered a separate sample category from storm drain samples, and therefore were not combined into the storm drain category. There are not enough combined sewer water samples for separate evaluation, and therefore Study 38 will not be considered further.

2.1 Gas Chromatography Columns

The vast majority of the data appear to have been analyzed using an SPB-octyl column. The SPB-octyl column resolves PCB-4 and PCB-10 into separate peaks, while the many columns that are equivalent to the DB-5 column do not. Because PCB-4 is the first congener (numerically and in terms of retention time) that coelutes on the DB-5 column but not on the SPB-octyl column, a quick way to determine which column was used is to look at whether PCB-4 is resolved. For the SGE-HT8 column, the first coelution pattern that is different from both the SPB-octyl and DB-5 is the coelution of PCB-20 and PCB-33.

The SPB-octyl column typically measures all 209 PCBs in 160 peaks. Of these, about 90 are detected in most samples; these 90 typically account for over 99 percent of the total PCB mass in most samples. These 90 congeners will be targeted in the factor analysis, but this list will be revised if the number of samples is less than 90 or if certain congeners (e.g., PCB-11, PCB-209) are present; these are obvious outliers and including them in the factor analysis would not provide additional useful information. In addition, the congener list for factor analysis may be slightly different for each environmental matrix. For example, high molecular weight congeners are rarely detected in air, even though they may be quite abundant in sediment. Every attempt will be made to use the same congener list across all media to provide the maximum degree of comparability of model results.

Even when the SPB-octyl column was used, there were slight differences in coelution patterns, but these are minor and can be rectified without losing too much information. Note that, in many studies that used the SPB-octyl column, PCB-107 coelutes with PCB-124. This coelution reduces the standard list of 90 peaks to only 89 peaks, although still representing 136 PCB congeners.

*PCB Congener Study Phase 2 – Initial Data Assessment***Table 3. Summary of Samples Available from Each Study in Each Medium**

Medium	Study Code	Number of Samples¹	Column Used	Detection Limits?	Surrogate Recovery Data?	Number of Field Blank Samples²
Air Deposition						
Air deposition	16	49	SPB-octyl	yes	no	1
Air deposition	39	15	SPB-octyl	yes	no	none
Total air deposition samples		64				1
Surface Water						
Surface water	6	57	SPB-octyl	yes	no	none
Surface water	12	6	SPB-octyl	yes	no	1
Surface water	13	21	SPB-octyl	yes	no	10
Surface water	14	56	SPB-octyl	yes	no	1
Surface water	15	24	SPB-octyl	yes	no	1
Surface water	22	3	DB-5	yes	yes	none
Surface water	23	51	SPB-octyl	no	no	none
Total surface water samples		218				13
Sediment						
Bed sediment	5	9	SPB-octyl	yes	yes	none
Bed sediment	6	17	SPB-octyl	yes	no	none
Suspended solids/bed sediment	12	14	SPB-octyl	yes	no	2
Suspended solids/bed sediment	13	32	SPB-octyl	yes	no	none
Bed sediment	22	2	DB-5	yes	yes	none
Bed sediment	27	7	SPB-octyl	yes	no	none
Suspended solids	40	68	SGE-HT8	Yes	no	none
Total sediment samples		149				2
Tissue						
Fish/shellfish	6	29	SPB-octyl	yes	no	none
Fish and crab	9	52	SPB-octyl	no	no	none
Fish	17	6	SPB-octyl	yes	no	none
Fish	18	7	SPB-octyl	no	no	none
Fish/shellfish	19	17	SPB-octyl	no	no	none
Clam and benthic invertebrates	26	17	SPB-octyl	no	no	none
Total tissue samples		111				none
Storm Drains						
Storm drain water	20	15	SPB-octyl	yes	yes	1
Storm drain water	21	25	DB-5	yes	yes	2
Storm drain solids	21	30	DB-5	yes	yes	none
Storm drain water	22	1	DB-5	yes	yes	none
Storm drain solids	22	4	DB-5	yes	yes	none
Total storm drain samples		75				3

1 – Includes field replicates

2 – Includes equipment blanks and trip blanks

2.2 Blanks

All studies appear to have been corrected for PCBs in the method blanks by changing the data qualifier code to ‘U’ for samples with concentrations less than five times that in the associated method blank. Information about other blanks (e.g., trip or field blanks) was reported for some studies. In many cases, the actual concentrations (or masses) of PCBs in the blanks were not reported; instead, only qualitative statements were made in the supporting documentation. In general, correction for field blanks has not been performed.

For two of the water studies (Studies 14 and 15), it appears that significant PCB contamination was introduced to the samples via the use of silicone rubber tubing. Silicone rubber has been shown to contain a variety of PCB congeners, especially PCB-45, -47, and -68 (Perdih and Jan 1994). For one other water study (Study 12), the vast majority of all reported concentrations were below detection limits, such that these data cannot be used during the factor analysis phase of this project. These issues are discussed in more detail in Section 4.0.

2.3 Surrogate Recoveries

Detailed information about surrogate recoveries is available only for Study 5 (sediment), Study 20 (storm drain water), Study 21 (storm drain water and storm drain solids), and Study 22 (surface water, sediment, storm drain water, and storm drain solids). These surrogate recoveries can be used to calculate uncertainty for the water and solids samples, with the assumption that this uncertainty applies to all samples in each category, regardless of study number. For air and tissue, it may be possible to estimate uncertainty from samples analyzed in duplicate.

3.0 Air Deposition Data

3.1 Data Summary

Two studies (Study 16 and Study 39) reported PCB data from atmospheric deposition. Air deposition sampling locations are shown on Figures 1 and 2. Both studies used the SPB-octyl column; therefore, the data are fully compatible and comparable between the two. Detection limits were provided for all peaks in all samples, with a few small exceptions (see Section 3.5). Of the 64 samples available, three from Study 16 were field duplicates. These three sets of duplicates could be used to estimate uncertainty for the purposes of factor analysis. Results from both studies are presented as mass flux in units of ng/m²/day (nanograms per square meter per day).

3.2 Blanks

All air data have already been corrected for method blank contamination. PCB-68 is detected in a few samples, but at very low levels, thus suggesting that contamination from silicone rubber tubing is not an issue with the air data set. No field blanks were available for air samples.

3.3 Obvious Patterns

Low molecular weight congeners have higher vapor pressures and, therefore, are expected to be abundant in atmospheric deposition samples. Thus, it is not surprising that PCB-11 is detected in 35 of the 64 samples. PCB-12+13 (which can also be associated with inadvertent PCBs) were detected in 25 samples. PCB-12 was, likewise, detected in samples from the Integrated Atmospheric Deposition Network, which monitors the Great Lakes region. In that data set, PCB-12 was not well correlated with any of the other congeners/peaks (Rodenburg and Meng 2013).

No obvious correlations were observed between PCB-11, -35, and -77, thus suggesting that pigments are not important sources of PCB-35 and PCB-77. As is typical, PCB-11 was not well correlated with any of the other PCB congeners/peaks. Eleven samples contained PCB-11 at over 5 percent of total PCB congeners; on average, PCB-11 makes up 2 percent of the total. The highest proportions of PCB-11 (at 8 to 9 percent of the total) were observed at the two Kent sampling stations, and at the 4401 East Marginal Way S location (CER_Duwamish).

PCB-209 was detected in 42 samples, which is surprisingly high because PCB-209 has such a low vapor pressure. PCB-206, -208, and -209 are strongly correlated, suggesting a source related to titanium chloride manufacture or the use of titanium dioxide pigment. The sum of PCB-206, 208, and 209 was over 5 percent of total PCB congeners in four samples, and as high as 12 percent. The highest proportions of PCB-206, -208, and -209 (11 to 12 percent of the PCB congener total) were observed at the South Park, East Marginal Way S, and Enumclaw sampling locations.

The comparison of the congener patterns of each sample versus Aroclors suggests that they most closely resemble Aroclors 1254 and 1260, which is surprising because these are high-molecular weight Aroclors with low vapor pressures.

3.4 Suitability for Factor Analysis

The air data are suitable for factor analysis. The two air studies include a total of 64 samples; therefore, any factor analysis should be limited to 64 peaks. Using the 64 most-often detected peaks would include approximately 80 percent of all of the PCB mass in the data set and would result in a data matrix in which approximately 18 percent of the data points are below the detection limit. This is a high but acceptable number. The chosen list of 64 should exclude congeners such as PBC-11 and -206, -208, and -209 because they are known to be associated with pigments. These congeners make up another approximately 5 percent of the total PCB mass in the air samples. Thus, after factor analysis, sources of approximately 85 percent of the PCBs in the air would be addressed. The uncertainty matrix will be estimated from the relative percent difference for the three samples analyzed in duplicate.

4.0 Surface Water Data

4.1 Data Summary

Seven studies reported PCB data from surface water samples. Surface water sampling locations are shown on Figures 3 and 4. ‘Water’ refers to whole water (i.e., the dissolved and particle phases). Six of these studies used the SPB-octyl column in a total of 215 samples. Study 22 used the DB-5 column in 3 samples. The Study 22 samples were eliminated from the PMF input matrix to eliminate the need for to resolve peaks from two different columns. Detection limits were provided for all except Study 23. Of the 218 available surface water samples, 21 were field duplicates from various studies.

The surface water data set contains a high number of below-detection-limit values across all studies, but especially for Study 12. Of the 215 SPB-octyl samples, more than 100 have fewer than 40 peaks above the detection limits. Ideally, these approximately 100 samples should be discarded from the data matrix, which would result in the exclusion of all samples from Studies 12 (6 samples) and 15 (24 samples). The Study 12 sample locations are the same as the Study 13 samples, and therefore elimination of the Study 12 data would not impact the geographic representativeness of the dataset. Study 15, however, represents samples collected from three locations, all upstream of RM 55. These are the only samples collected in the upper Middle Green and Upper Green subwatersheds. Therefore, Study 15 will be retained for factor analysis even though there are a large number of non-detects. Since it is desirable to keep as many samples as possible from Study 15, the result will be an input data matrix with a high number of non-detects, i.e., more than 25 percent of all data points.

4.2 Blanks

Most surface water sample results have been corrected for method blank contamination, but not for field blank contamination. Congener-specific concentrations in blanks from Studies 14 and 15 indicate a relatively high concentration of PCB-68, which is an indicator of contamination from silicone rubber. In agreement with the blank concentrations, PCB-68 is detected in many samples from these two studies. PCB-68 comprises, on average, 20 percent of the sum of PCBs (non-detects set to zero) in samples from Studies 14 and 15. In all other samples, PCB-68 comprises, on average, much less than 1 percent of the sum of PCBs. In the samples from these two studies, many congeners/peaks are correlated with PCB-68 (Table 4), especially PCB-44+47+65 and PCB-45+51, which are also known to be associated with silicone rubber. Contamination from silicone rubber tubing is, therefore, a major problem in water samples from these two studies.

Ideally, blank correction would be performed, but because only one field blank was collected for each of these studies, blank correction may not be possible. The concentrations of PCB-68, 44+47+65 and PCB-45+51 are highly variable in these samples, suggesting that blank correction using one constant concentration of each congener could do more harm than good. Instead, data from Studies 14 and 15 will be entered into the PMF model without blank correction, because the model is expected to generate a factor that describes the silicone rubber tubing

PCB Congener Study Phase 2 – Initial Data Assessment

contamination, and the concentration of this factor will vary among the samples from Study 14 and 15.

Table 4. Congeners/Peaks that are Most Closely Correlated with PCB-68 in Water Samples from Studies 14 and 15

Congener	R ²
PCB-44/47/65	0.863
PCB-45/51	0.797
PCB-25	0.568
PCB-21/33	0.540
PCB-17	0.478
PCB-49/69	0.224
PCB-32	0.189
PCB-179	0.133
PCB-50/53	0.120
PCB-16	0.118
PCB-2	0.092
PCB-88/91	0.085
PCB-42	0.071
PCB-22	0.070
PCB-198/199	0.069
PCB-136	0.063
PCB-197/200	0.057
PCB-190	0.056
PCB-159	0.055
PCB-203	0.052
PCB-11	0.049

All congeners/peaks with R² > 0.05 are shown.

PCB = Polychlorinated biphenyl.

R² = Coefficient of determination from linear regression of the concentrations of each congener versus those of PCB-68.

Another problem is what to do with studies for which no field blank information is available, or for which quantitative blank data are available, but blank correction has not previously been performed. Because the Study 14 and 15 data are proposed to be included without blank correction, it is recommended that blank correction not be performed on any of the other surface water data. The only other option is to blank-correct some studies but not others, and this may introduce systematic changes in congener patterns that may prevent the PMF program from finding similar congener patterns across more than one study.

4.3 Obvious Patterns

PCB-11 is sometimes as much as 15 percent of the sum of PCBs, but, on average, it is less than 1 percent. This congener made up over 5 percent of the sum of PCBs in two samples: 3373 and 3375, both collected from the Foster Links cart bridge during Study 13.

PCB-206, -208, and -209 are similar; they constitute up to 27 percent of the sum of PCBs, but, on average, they are less than 2 percent. These congeners made up over 5 percent of the sum of PCBs in 13 surface water samples.

Comparison of the congener patterns of each sample versus the Aroclors suggests that they most closely resemble Aroclors 1254 and 1260, but there is a great deal of variability. Many samples do not resemble any Aroclor. For Studies 14 and 15, this may be due to blank contamination, which does not resemble an Aroclor congener pattern. For some samples, this may be due to a very high number of non-detects. For other samples, it is possible that the congener pattern does not resemble any Aroclor because pigment sources or microbial dechlorination might dominate the congener pattern.

4.4 Suitability for Factor Analysis

The surface water data are suitable for factor analysis. Since there are only three samples from Study 22, and these were analyzed using the DB-5 column, the Study 22 surface water samples will be excluded from the PMF matrix so that all data will be from the SPB-octyl column and no summing of congeners will be required. As a result, the maximum amount of data available for modeling is 89 congeners⁴ is 218 samples. In such a matrix, almost 60 percent of the data points would be below detection. Therefore, the number of congeners and samples will need to be reduced in order to construct a PMF input file with a reasonable number of non-detects, such as 25 percent. To reach this, the PMF input will be trimmed to approximately 77 peaks in about 90 samples. The uncertainty matrix will be estimated from the surrogate recoveries from Studies 20 and 21.

⁴ Note that PCB-207 coelutes with PCB-124.

5.0 Sediment Data

5.1 Data Summary

Sediment samples include bed sediment and suspended sediment. Sediment sampling locations are shown on Figures 5 and 6. Samples in this category were generated from seven studies. Five of the studies used the SPB-octyl column, one used the DB-5 column (Study 22) and one used the SGE-HT8 column (Study 40). The dataset includes a total of 144 samples, including nine field duplicates. Detection limits were provided for all studies. Because Study 22 includes only two sediment samples, these will be eliminated from the sediment dataset. This will limit the dataset to only two columns (SPB-octyl and SGE-HT8).

5.2 Blanks

The vast majority of the sediment data have already been corrected for method blank contamination but not for field blank contamination. Sediment collection methods are quite simple and the concentrations are high, such that blank correction is rarely necessary. Because tubing is usually not required to collect sediment samples, contamination from silicone rubber tubing is unlikely. Thus, it is not surprising that PCB-68 is detectable in many samples but never comprises more than 1 percent of the sum of PCBs. Therefore, it is recommended that the solids data be entered into the PMF model without (further) blank correction.

5.3 Obvious Patterns

The correlation matrix shows three zones of high correlation for low, medium, and high molecular weight congeners. This suggests that the three Aroclors (probably 1242/1248, 1254, and 1260) are dominant contributors to the sediment PCB burden. The Aroclor regressions suggest that most samples resemble Aroclors 1254 and 1260.

5.4 Suitability for Factor Analysis

Sediment includes ambient bed sediment and suspended sediment. The two samples from Study 22 in which PCBs were measured on a DB-5 column will be discarded from the PMF input, as described above. The data matrix resulting from rectifying the SPB-octyl and SGE-HT8 congener patterns will result in 80 peaks and 148 samples, in which about 10 percent of the data points are below detection, which is acceptable.

6.0 Storm Drain Data

6.1 Data summary

Three studies measured PCBs in storm drain water and storm drain solids. Sample locations are shown in Figure 7. This category comprises samples of whole water as well as solids. Normally we would seek to keep these types of samples separate, because solids can have a very different (usually higher molecular weight) PCB congener pattern than water samples. However, storm water discharge samples tend to have very high PCB concentrations as well as high suspended solids. Thus it is reasonable to assume that the overwhelming majority (perhaps >90%) of PCBs in these samples are sorbed to solids in the water. Therefore, combining water and solids data for storm water and storm drain solids should provide a coherent data set for which the PMF program can find a suitable solution.

There are not enough samples of storm drain solids to be analyzed as a separate PMF matrix. Thus the only alternative to combining them is to analyze the storm drain solids with the bed and suspended sediment. Because the PCB sources to storm drains could potentially be very different from the sources to the ambient bed sediment, it makes more sense to analyze the storm drain water and storm drain solids together as one matrix.

6.2 Blanks

All storm drain data have already been corrected for method blank contamination. Field blank data are available for most of the storm drain samples, but no field blank correction has been performed.

6.3 Obvious Patterns

PCB-11 is detected in approximately 55 of 75 samples, indicating that this low molecular weight congener is abundant in storm drain samples. It averages about 1 percent of total PCBs in these samples, with three samples that contain PCB-11 at over 5 percent of total PCBs (two collected at Northland Services, one at Puget Sound Coatings). It is not well correlated with other congeners/peaks. The congener patterns of most samples resemble Aroclors 1254 and 1260.

6.4 Suitability for Factor Analysis

The storm drain data are suitable for factor analysis. Because the storm drain data set contains results from both the SPB-octyl and DB-5 columns, the combined data set will have 73 peaks in 75 samples. One sample (Sample 625) has a high number of non-detects and will be discarded, leaving 73 peaks in 74 samples in a data set with 14% non-detects, which is acceptable.

7.0 Tissue Data

7.1 Data Summary

Six studies reported PCB data in tissues from fish, shellfish, and invertebrates. All studies appear to have used the SPB-octyl column; therefore, all data are internally consistent and comparable. There are a total of 128 tissue samples. Seven samples were analyzed in duplicate. Detection limits are available only for Study 6 (29 samples) and Study 17 (6 samples).

7.2 Blanks

Most of the tissue data have already been corrected for method blank contamination. Generally, PCB concentrations in tissue are high and sample handling is minimal; therefore, field blank correction is usually not required for tissue samples. Thus, it is recommended that tissue data be entered into the PMF model without blank correction. PCB-68 is frequently detected but never comprises more than 1 percent of the sum of PCBs in tissue samples.

7.3 Obvious Patterns

PCB-11 is detected in approximately 40 percent of samples, indicating that this low molecular weight congener is accumulating in biota. PCB-11 was similarly detected in biota from the Portland Harbor Superfund Site (data available on EPA's STOrage and RETrieval system [STORET]). It is not well correlated with other congeners/peaks. The congener patterns of most samples resemble Aroclors 1254 and 1260.

7.4 Suitability for Factor Analysis

The tissue data are suitable for factor analysis. All 128 samples can be included in the data matrix of 90 peaks, resulting in an input matrix with 3.5 percent of data points below detection limits, which is very good.

8.0 Conclusions and Proposed Methodology

In general, the data quality is good. Future data collection could be easily enhanced by the adoption of better data management practices at almost no cost, as described in Section 8.0. Other recommendations would enhance data quality via techniques that might entail some modest costs, such as changing the water sampling methods to allow more congeners/peaks to be detected. Nevertheless, the data are of sufficient quality to allow factor analysis to be performed on all four subsets of media (i.e., air, water, sediment, and tissue).

Across all four of these media, the congener patterns most often resemble Aroclors 1254 and 1260. However, non-Aroclor sources are also apparent, because congeners such as PCB-11 and PCB-209 are frequently detected in all media. In this respect, the Duwamish-Green River is similar to other United States waterways, including the Delaware River, New York/New Jersey Harbor, and the Portland Harbor Superfund Site, where Aroclors are the main PCB sources but non-Aroclor sources are also relevant.

Table 5 summarizes the number of samples available for factor analysis for the four media. All samples are of high-enough quality to be included in the factor analysis for air, sediment, storm drains, and tissue media. For surface water, a large number of samples (more than 100) must be excluded from factor analysis due to a high number of below-detection-limit values.

Table 5. Number of Samples Available for Factor Analysis by Medium and the Percent of Data Points that will be Below Detection Limits in the Input Matrix

Medium	Number of Samples	Number of Peaks	Percent Below Detection Limit	Note
Air Deposition	64	64	18	Number of peaks is limited by the number of samples available
Surface Water	115	69	37	If all samples are used, 46 percent of data points are below detection limits
Sediment	148	80	10	
Storm Drains	74	73	14	Number of peaks is limited by the number of samples available.
Tissue	128	90	3.5	

8.1 Treatment of Non-Detects

In the PMF input, non-zero values must be given for values that are below the Limit of Detection (LOD). There are several approaches to assigning these proxy values. One approach is to assign a value of one-half the detection limit. This works well when relatively few data points are below detection. Another option is to assign a random value between 0 and the detection limit. This is preferred when the data sets contain large percentages of non-detect values. Given the relatively high proportion of non-detects in the LDW data sets, a random value between zero and the detection limit will be used via the following function in Excel:

$$\text{Proxy} = \text{LOD} * \text{RANDBETWEEN}(1,100)/100$$

PCB Congener Study Phase 2 – Initial Data Assessment

In cases where the LODs are not known, the lowest detected concentration by homolog will be assumed to be the LOD. When no congeners within a homolog are detected, the lowest detected concentration of the homolog with one fewer chlorine atom will be used. When the lowest detected concentration appears quite high compared to other homologs within the same sample the lowest detected concentration of the homolog with one fewer chlorine atom will again be used.

Other methods for assigning proxy concentrations are available, such as linear regression on order statistics (ROS). However, regressions would need to be developed for each congener peak in each matrix; in some cases, insufficient detected concentrations are available. Because the level of effort involved in this method is much higher, initial model runs will be performed using the random value method above. Large uncertainty factors are applied to the non-detected values in PMF; the non-detects typically do not significantly impact the model results. If initial model runs indicate that this is likely to be an issue, ROS methods may be utilized.

9.0 Recommendations for Data Collection and Management Improvements

Based on examination of the data, the following recommendations are proposed:

- For all future data collection, specify that the contract laboratory must use the SPB-octyl column for Method 1668 analyses and must report the data using the standard SPB-octyl coelution pattern (e.g., the pattern specified in the Delaware River Basin Commission’s [DRBC’s] project-specific modifications to Method 1668).
- Contract laboratories should be required to use a standard electronic data deliverable (EDD) format for PCB congener results. This would allow all data to be seamlessly imported into a database (e.g., Microsoft Access), which would save a tremendous number of labor hours and would eliminate the possibility that mistakes are made during data importing from the various studies into the master database. In addition, it would result in a central database that could be easily transformed into the format required for input into Ecology’s Environmental Information Management (EIM) database. It is recommended that DRBC’s project-specific modifications to the Method 1668 EDD format be used as a starting point and modified as necessary. (Note that the PCB congener database being developed as part of this study used the DRBC framework and added relevant EIM fields.)
- Contract laboratories should be required to report detection limits for every peak in every sample and surrogate recoveries for every sample. DRBC’s EDD format includes this requirement.
- Blanks should be collected on a regular schedule, such as 1 blank for every 10 samples. Concentration data from all blanks (field, laboratory, equipment rinse, travel, etc.) should be reported with the results for the samples in the same EDD format. Blanks must be clearly marked as blanks so that they are not confused with samples.
- Particularly for water samples, detection limits need to be improved. For the few studies that measured water and reported detection limits, they appear to be reasonable at approximately 1 pg/L or less. Even in Study 12, in which very few congeners/peaks were detected, the detection limits are reported to be around 1 pg/L. Careful attention to sample collection can drive PCB concentrations in water sample blanks down to approximately 30 pg/L, which might allow a greater number of PCB congeners to be detected. Alternatively, collecting larger volume water samples can increase the mass of the PCB congeners in each sample, allowing a larger number of congeners to be above detection limits. These issues should be investigated.
- In the future, all water sampling should be conducted with Teflon tubing or other non-PCB containing material, and never with silicone rubber tubing. Platinum-cured silicone tubing may be substituted for the standard silicone flexible tubing needed in an autosampler or peristaltic pump (see also Leidos 2016b).

10.0 References

EPA (U.S. Environmental Protection Agency). 1999. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS.

Larsen, R.K. and J.E. Baker. 2003. Source Apportionment of Polycyclic Aromatic Hydrocarbons in the Urban Atmosphere: A Comparison of Three Models. *Environmental Science & Technology* **37**: 1873-1881.

Leidos. 2016a. Green-Duwamish River Watershed PCB Congener Study: Phase 1. Bothell, WA, Department of Ecology State of Washington Toxics Cleanup Program.

Leidos. 2016b. Technical Memorandum: Potential for PCB Contamination from Sampling Equipment Tubing Materials. Prepared by Leidos for Washington Department of Ecology. November 23, 2016.

Paatero, P. and U. Tapper. 1994. Positive Matrix Factorization: a Non-negative Factor Model with Optimal Utilization of Error Estimates of Data Values. *Environmetrics* **5**: 111-126.

Perdih, A. and J. Jan. 1994. Formation of polychlorobiphenyls in silicone rubber. *Chemosphere* **28**(12): 2197-2202.

Rodenburg, L.A. and Q. Meng. 2013. Source Apportionment of Polychlorinated Biphenyls in Chicago Air from 1996 to 2007. *Environmental Science & Technology* **47**(8): 3774-3780.

Figures

PCB Congener Study Phase 2 – Initial Data Assessment



Figure 1. PCB Congener Sampling Locations: Air Deposition



 leidos

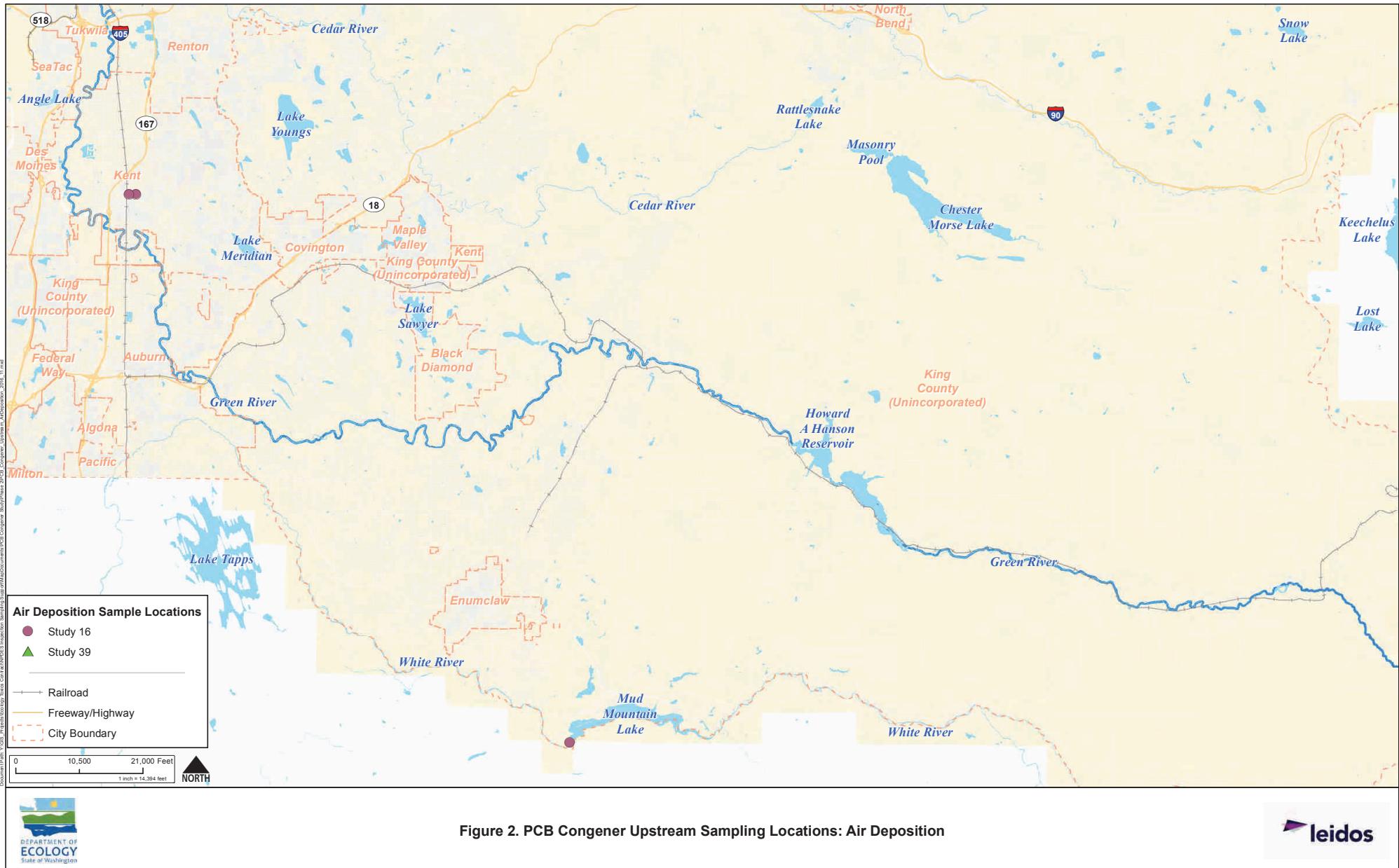


Figure 2. PCB Congener Upstream Sampling Locations: Air Deposition





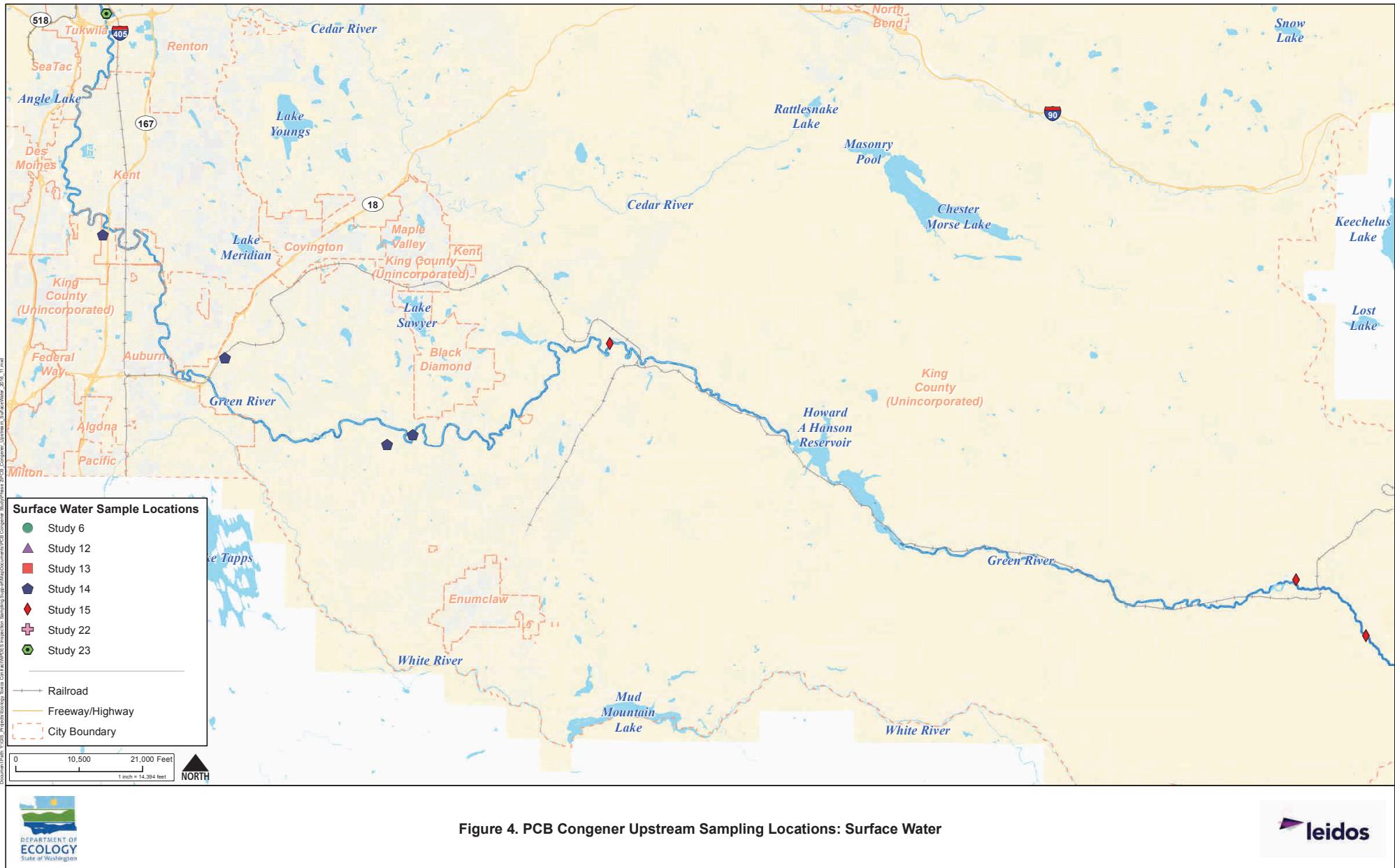


Figure 4. PCB Congener Upstream Sampling Locations: Surface Water

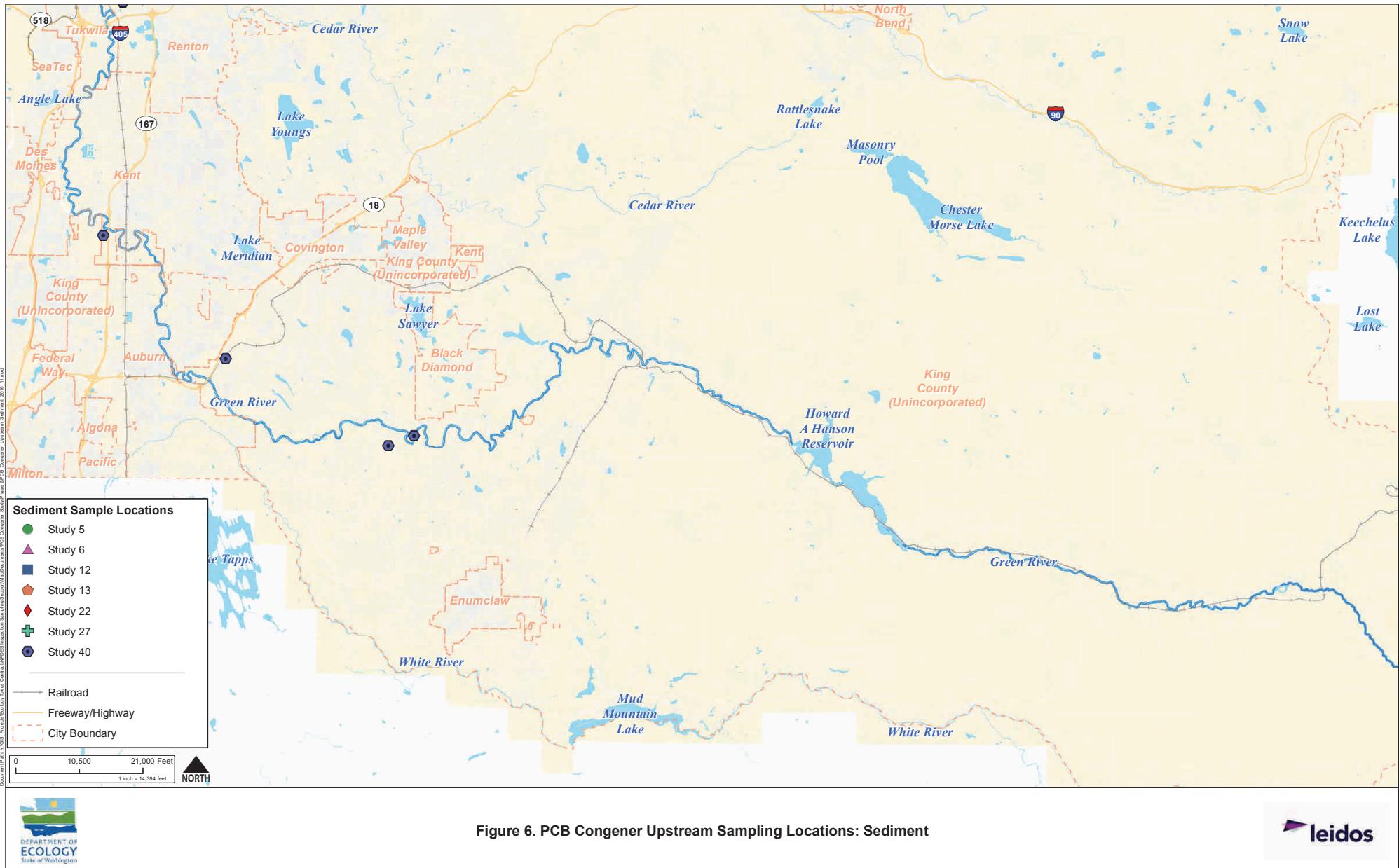




Figure 5. PCB Congener Sampling Locations: Sediment



 leidos



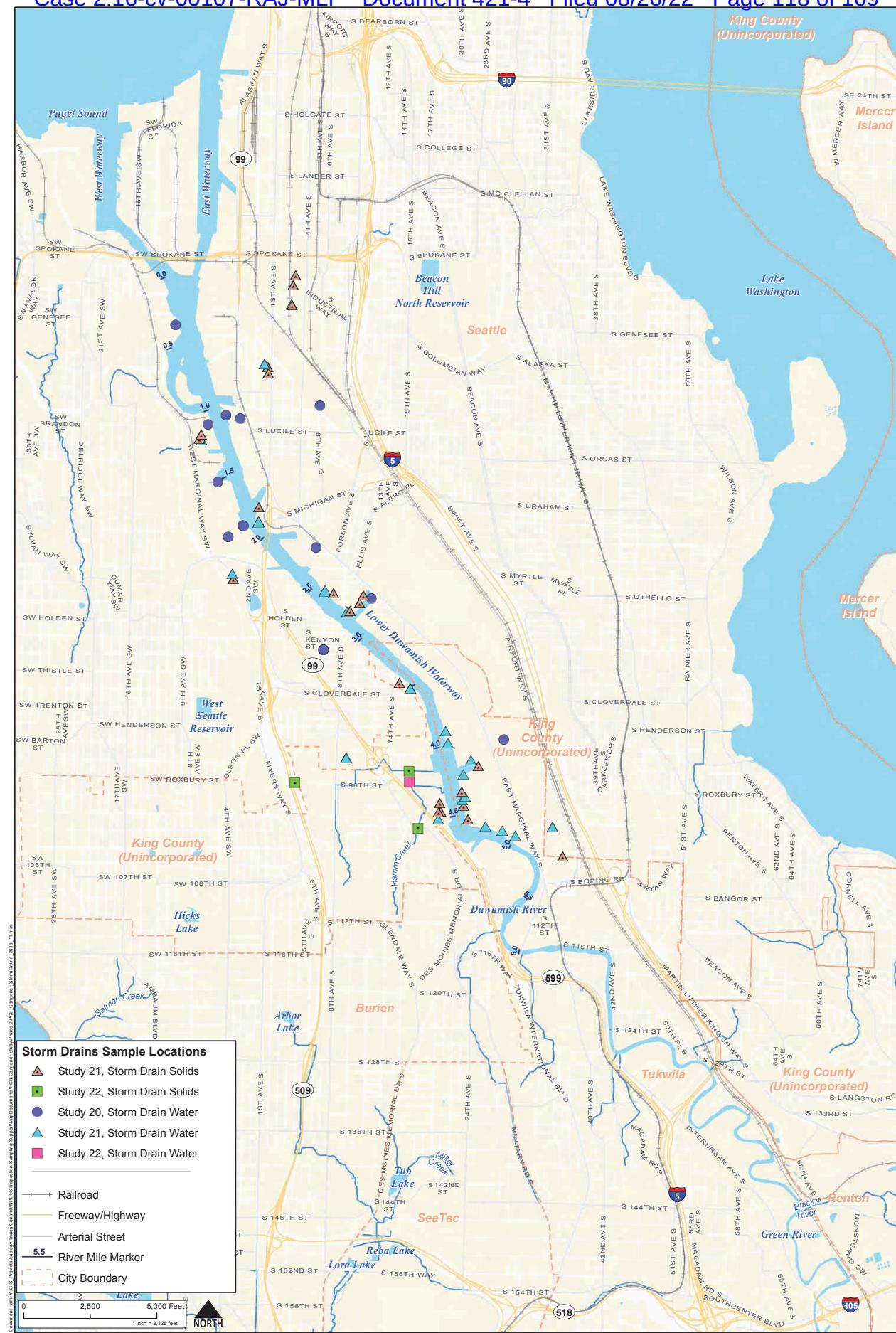


Figure 7: PCB Congener Sampling Locations: Storm Drains



 leidos

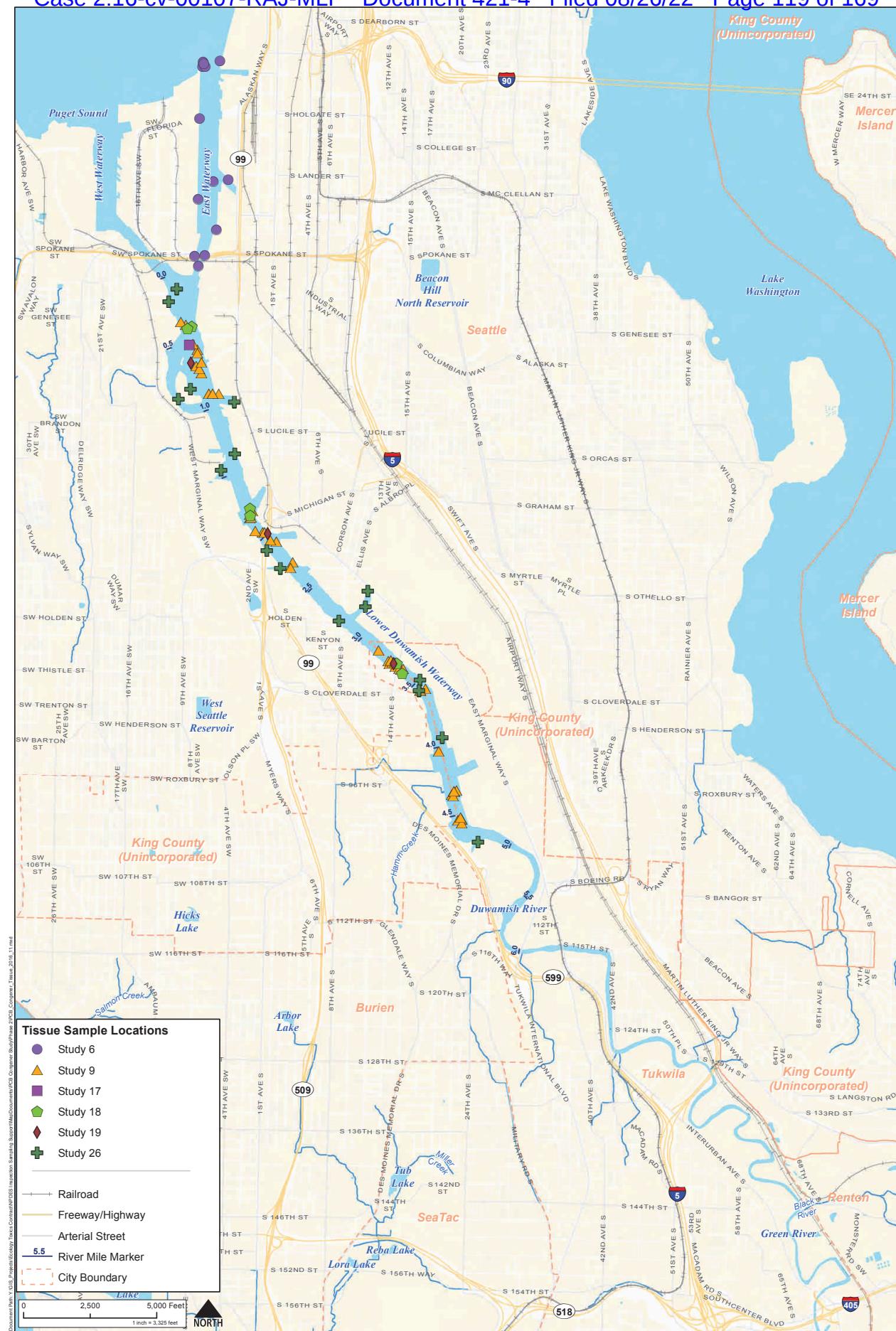


Figure 8: PCB Congener Sampling Locations: Tissue



 leidos

PCB Congener Study Phase 2 - Source Evaluation

Appendix B Spatial Distribution Maps

PCB Congener Study Phase 2 - Source Evaluation

List of Maps

Air Deposition

- Figure 1. PCB Concentrations in Air Deposition Samples, Factor 1 (Similar to Aroclor 1016/1242)
- Figure 2. PCB Concentrations in Air Deposition Samples, Factor 2 (Similar to Aroclor 1248)
- Figure 3. PCB Concentrations in Air Deposition Samples, Factor 3 (Similar to PCB-11 and mixed Aroclors)
- Figure 4. PCB Concentrations in Air Deposition Samples, Factor 4 (Not similar to any Aroclor)
- Figure 5. PCB Concentrations in Air Deposition Samples, Factor 5 (Similar to Aroclor 1254)
- Figure 6. PCB Concentrations in Air Deposition Samples, Factor 6 (Similar to Aroclor 1260)
- Figure 1a. PCB Concentrations in Air Deposition Samples, Factor 1 (Similar to Aroclor 1016/1242)
- Figure 2a. PCB Concentrations in Air Deposition Samples, Factor 2 (Similar to Aroclor 1248)
- Figure 3a. PCB Concentrations in Air Deposition Samples, Factor 3 (Similar to PCB-11 and mixed Aroclors)
- Figure 4a. PCB Concentrations in Air Deposition Samples, Factor 4 (Not similar to any Aroclor)
- Figure 5a. PCB Concentrations in Air Deposition Samples, Factor 5 (Similar to Aroclor 1254)
- Figure 6a. PCB Concentrations in Air Deposition Samples, Factor 6 (Similar to Aroclor 1260)

Sediment

- Figure 1. PCB Concentrations in Surface Sediment, Factor 1 (Similar to Aroclor 1016/1242)
- Figure 2. PCB Concentrations in Surface Sediment, Factor 2 (Similar to Aroclor 1248)
- Figure 3. PCB Concentrations in Surface Sediment, Factor 3 (Similar to Aroclor 1254)
- Figure 4. PCB Concentrations in Surface Sediment, Factor 4 (Similar to Non-Aroclor)
- Figure 5. PCB Concentrations in Surface Sediment, Factor 5 (Similar to Aroclor 1260)
- Figure 1a. PCB Concentrations in Upstream Surface Sediment, Factor 1 (Similar to Aroclor 1016/1242)
- Figure 2a. PCB Concentrations in Surface Sediment, Factor 2 (Similar to Aroclor 1248)
- Figure 3a. PCB Concentrations in Surface Sediment, Factor 3 (Similar to Aroclor 1254)
- Figure 4a. PCB Concentrations in Surface Sediment, Factor 4 (Similar to Non-Aroclor)

- Figure 5a. PCB Concentrations in Surface Sediment, Factor 5 (Similar to Aroclor 1260)

Surface Water

- Figure 1. PCB Concentrations in Surface Water, Factor 1 (Similar to Aroclor 1216)
- Figure 2. PCB Concentrations in Surface Water, Factor 2 (Similar to Aroclor 1248)
- Figure 3. PCB Concentrations in Surface Water, Factor 3 (Similar to Aroclor 1254)
- Figure 4. PCB Concentrations in Surface Water, Factor 4 (Similar to Aroclor 1260)
- Figure 1a. PCB Concentrations in Surface Water, Factor 1 (Similar to Aroclor 1216)
- Figure 2a. PCB Concentrations in Surface Water, Factor 2 (Similar to Aroclor 1248)
- Figure 3a. PCB Concentrations in Surface Water, Factor 3 (Similar to Aroclor 1254)
- Figure 4a. PCB Concentrations in Surface Water, Factor 4 (Similar to Aroclor 1260)

Tissue

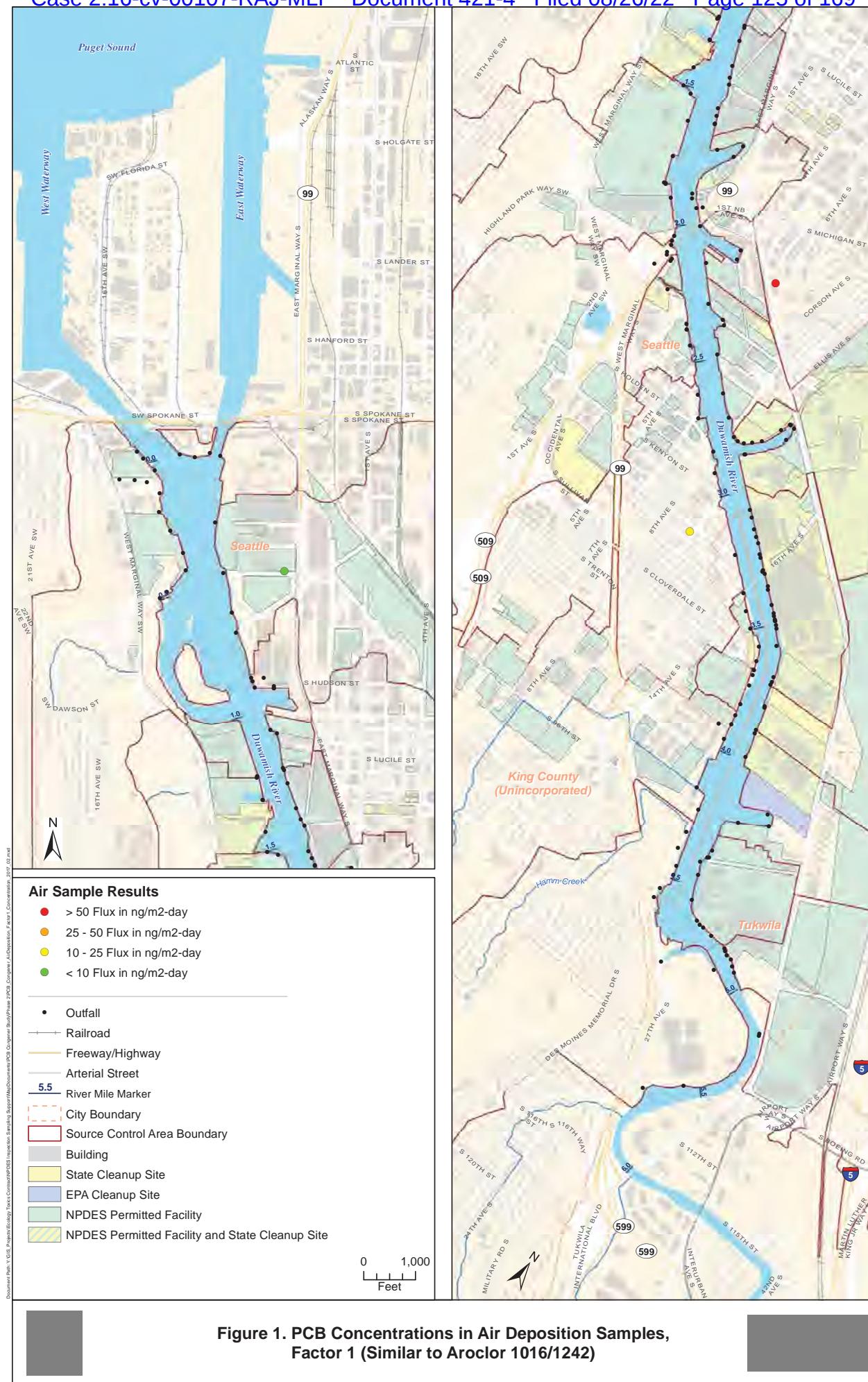
- Figure 1. PCB Concentrations in Tissue, Factor 1 (Similar to weathered Aroclor 1248)
- Figure 2. PCB Concentrations in Tissue, Factor 2 (Similar to Aroclor 1254)
- Figure 3. PCB Concentrations in Tissue, Factor 3 (Similar to weathered mix of Aroclors)
- Figure 4. PCB Concentrations in Tissue, Factor 4 (Similar to weathered Aroclor 1260)
- Figure 5. PCB Concentrations in Tissue, Factor 5 (Similar to Aroclor 1260)

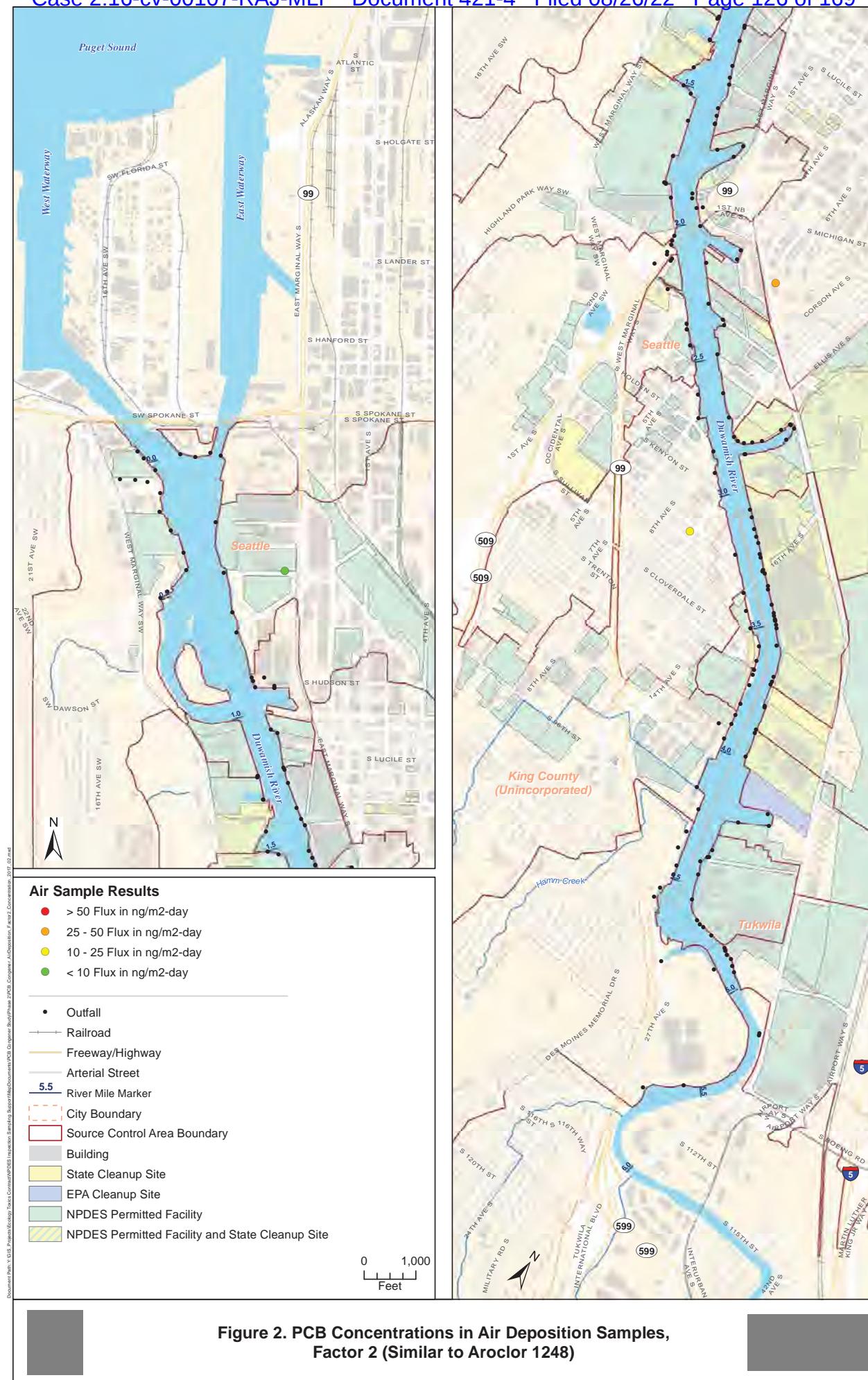
Storm Drains

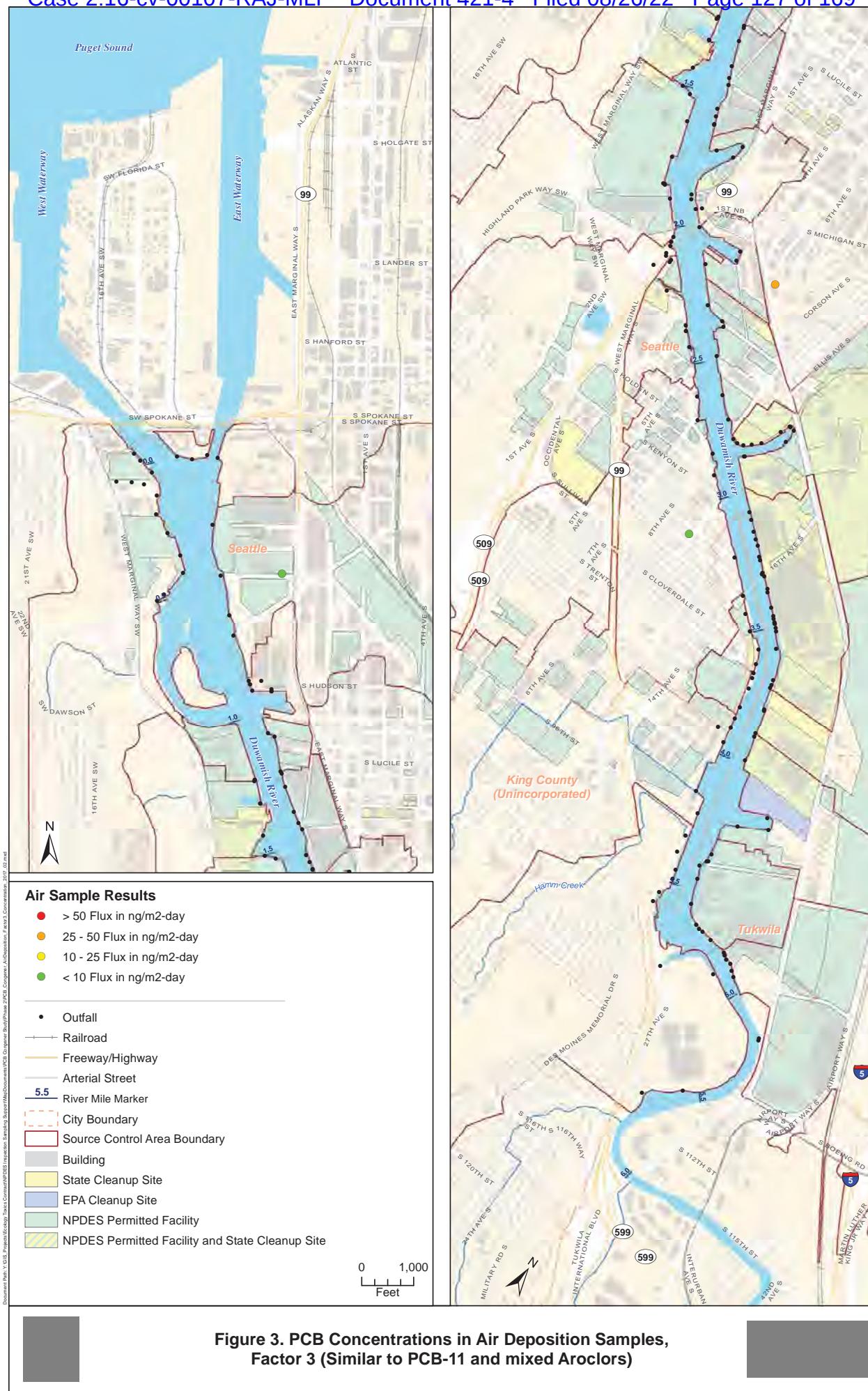
- Figure 1. PCB Concentrations in Storm Drains, Factor 1 (Similar to Aroclor 1016/1242)
- Figure 2. PCB Concentrations in Storm Drains, Factor 2 (Similar to Aroclor 1248)
- Figure 3. PCB Concentrations in Storm Drains, Factor 3 (PCB-11 and mixed Aroclors)
- Figure 4. PCB Concentrations in Storm Drains, Factor 4 (Similar to Aroclor 1254)
- Figure 5. PCB Concentrations in Storm Drains, Factor 5 (Similar to Aroclor 1260)
- Figure 6. PCB Concentrations in Storm Drains, Factor 6 (PCB-209 and not similar to Aroclors)

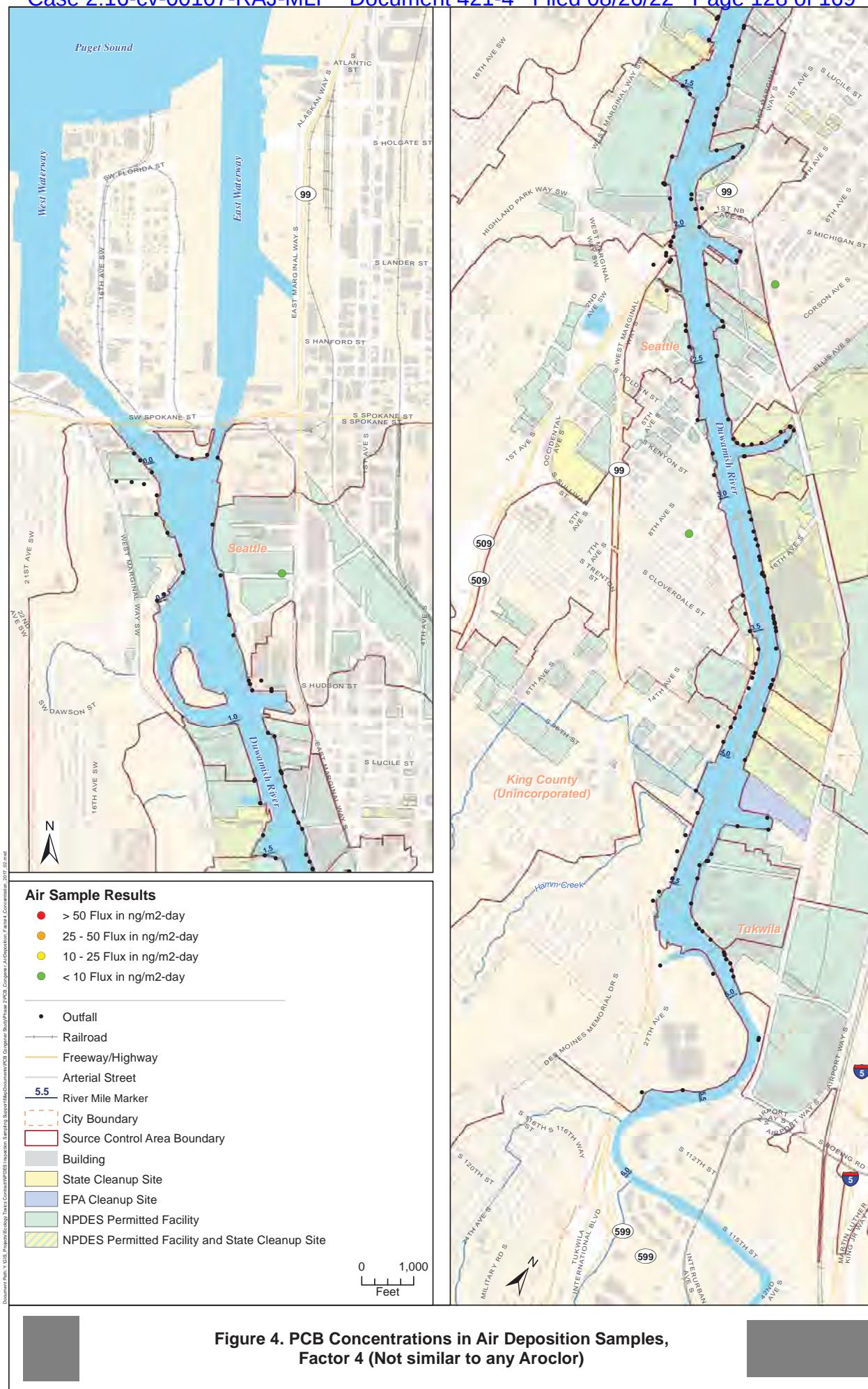
PCB Congener Study Phase 2 - Source Evaluation

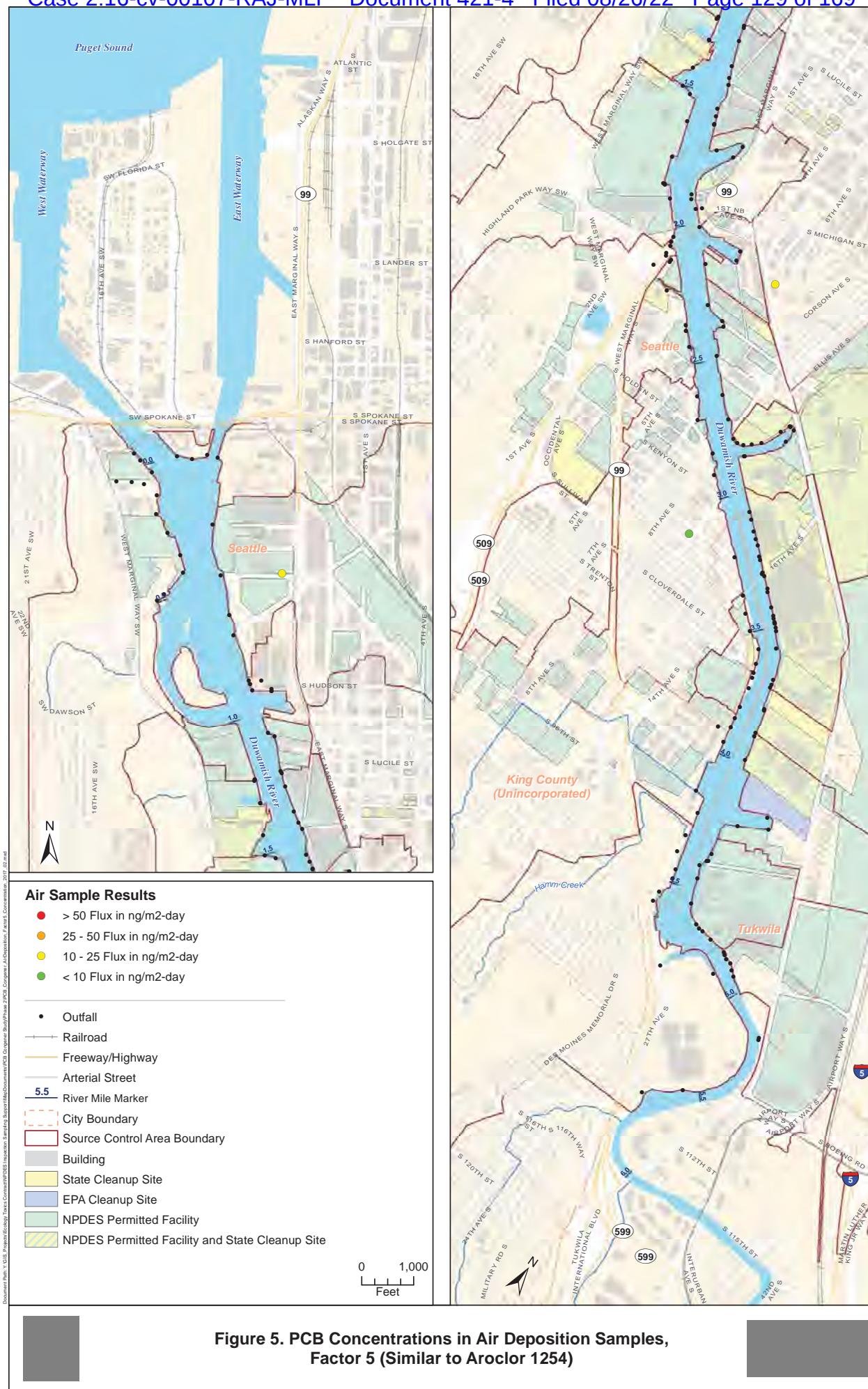
PCB Concentrations in Air Deposition Samples

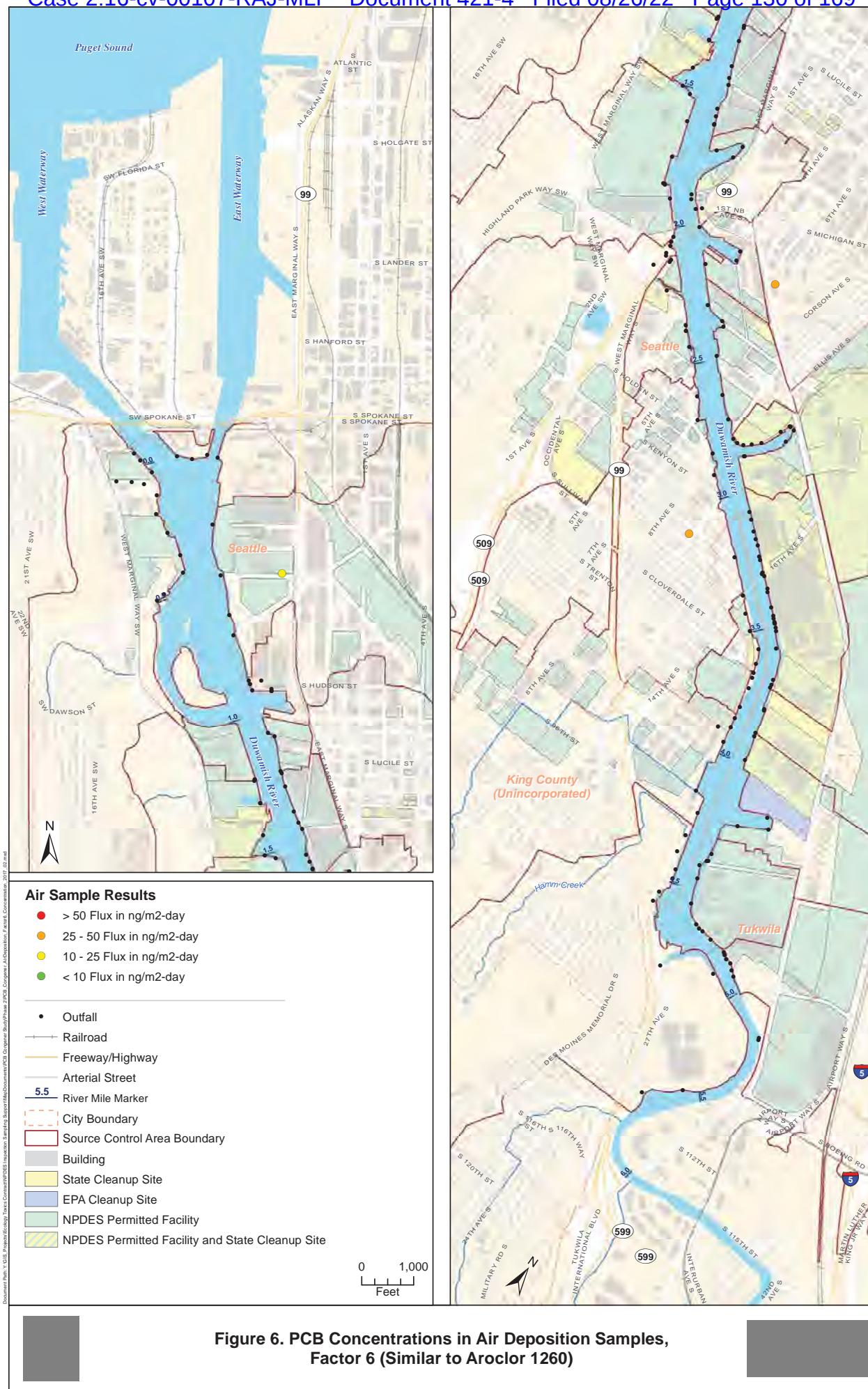




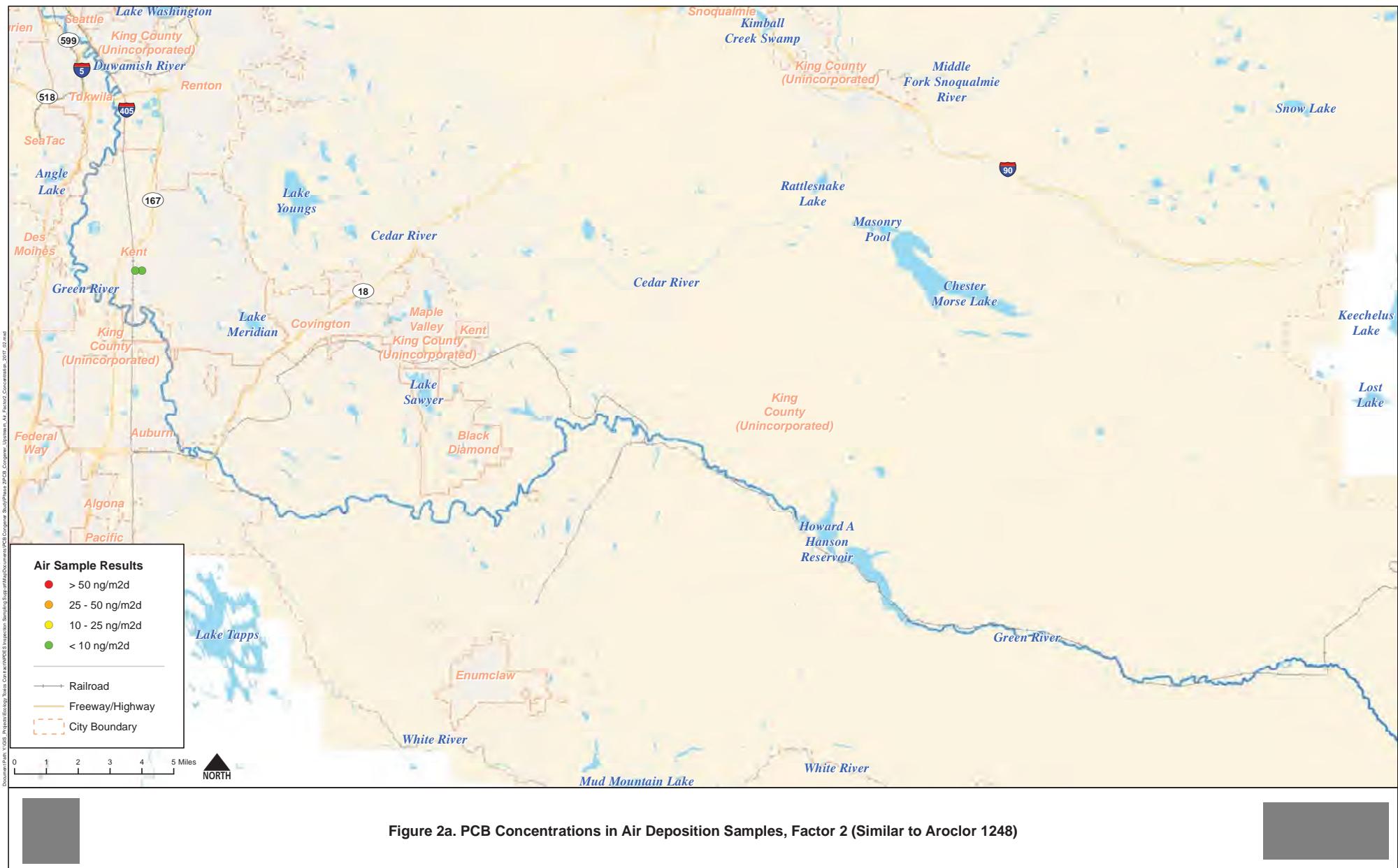


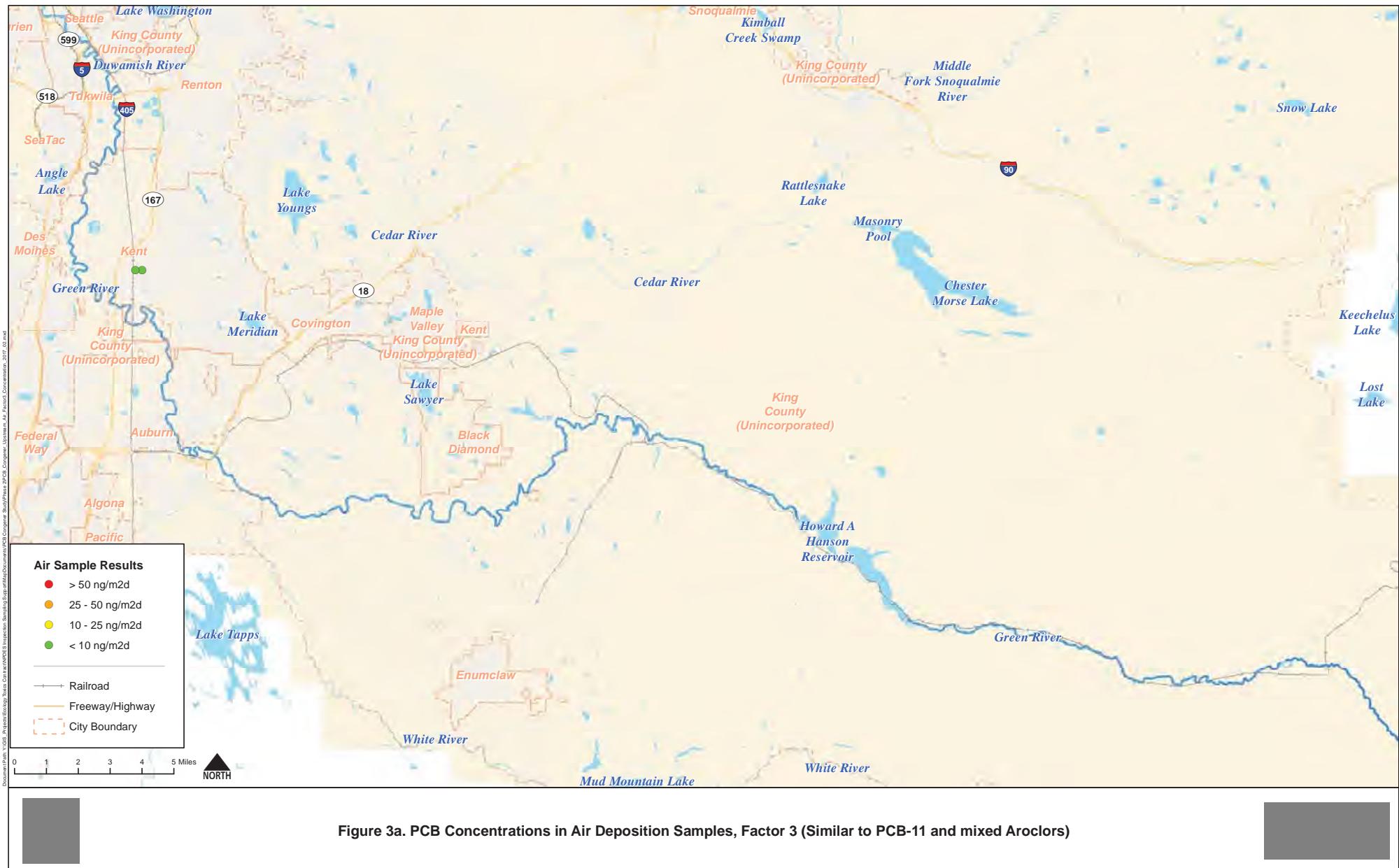


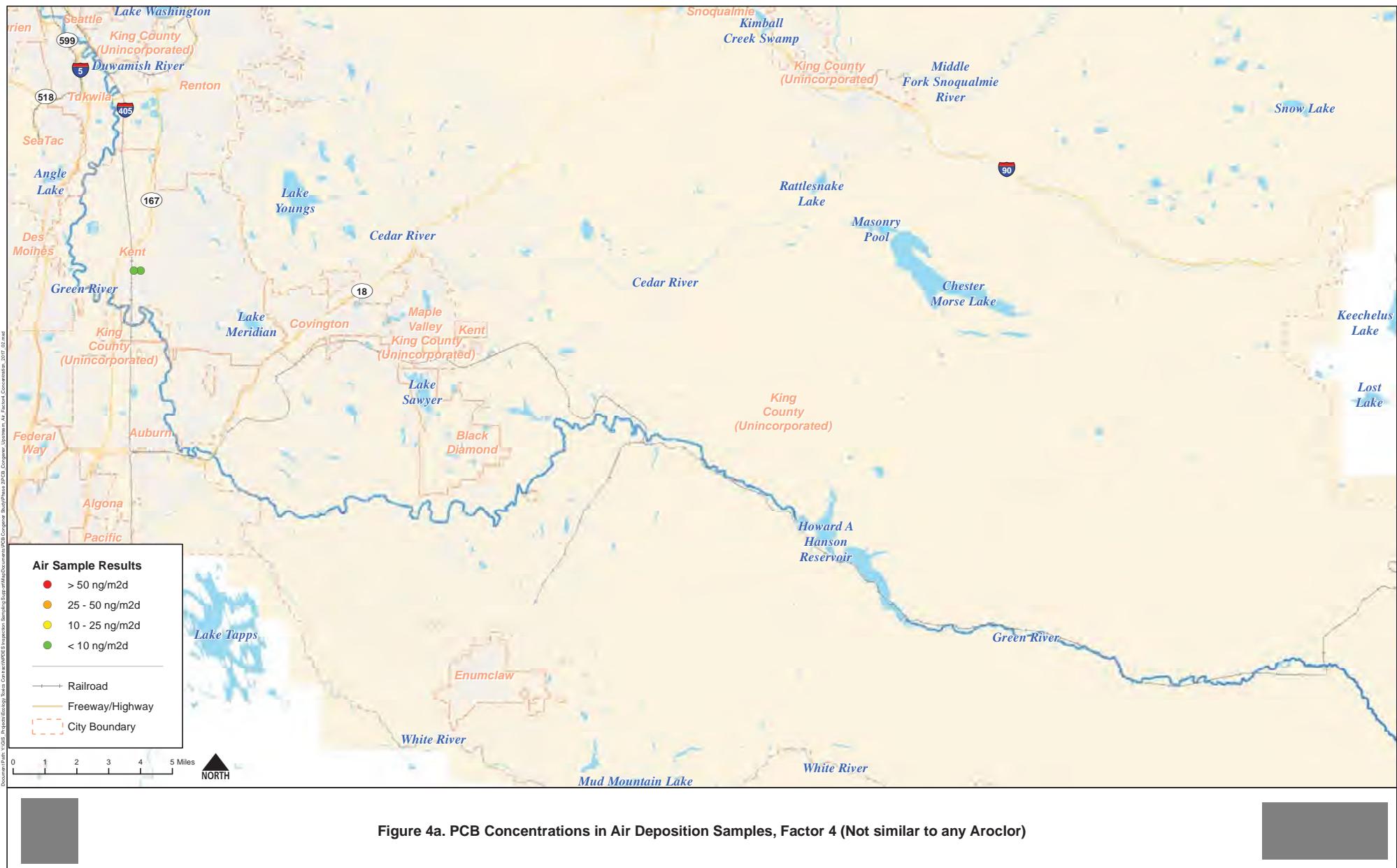


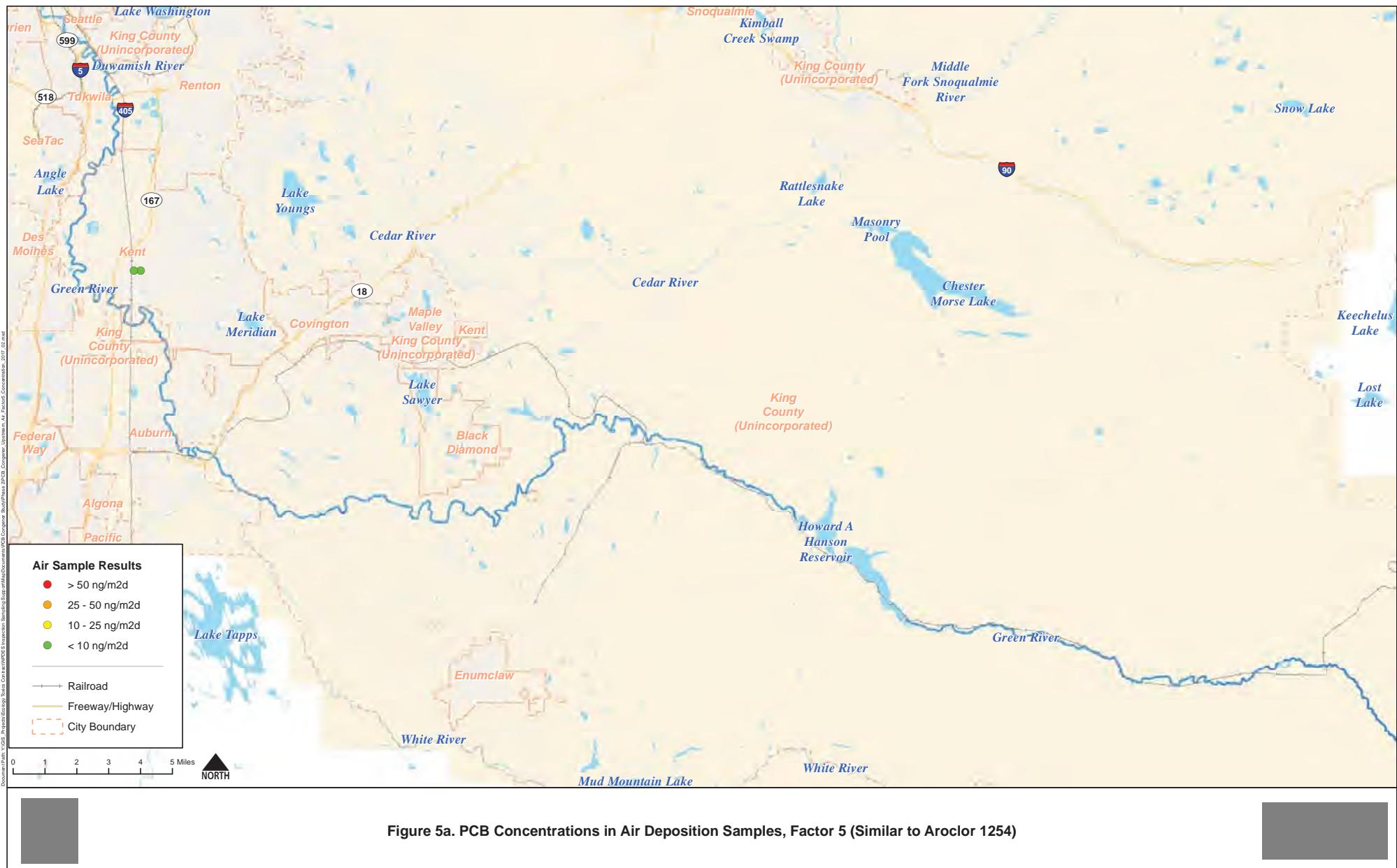


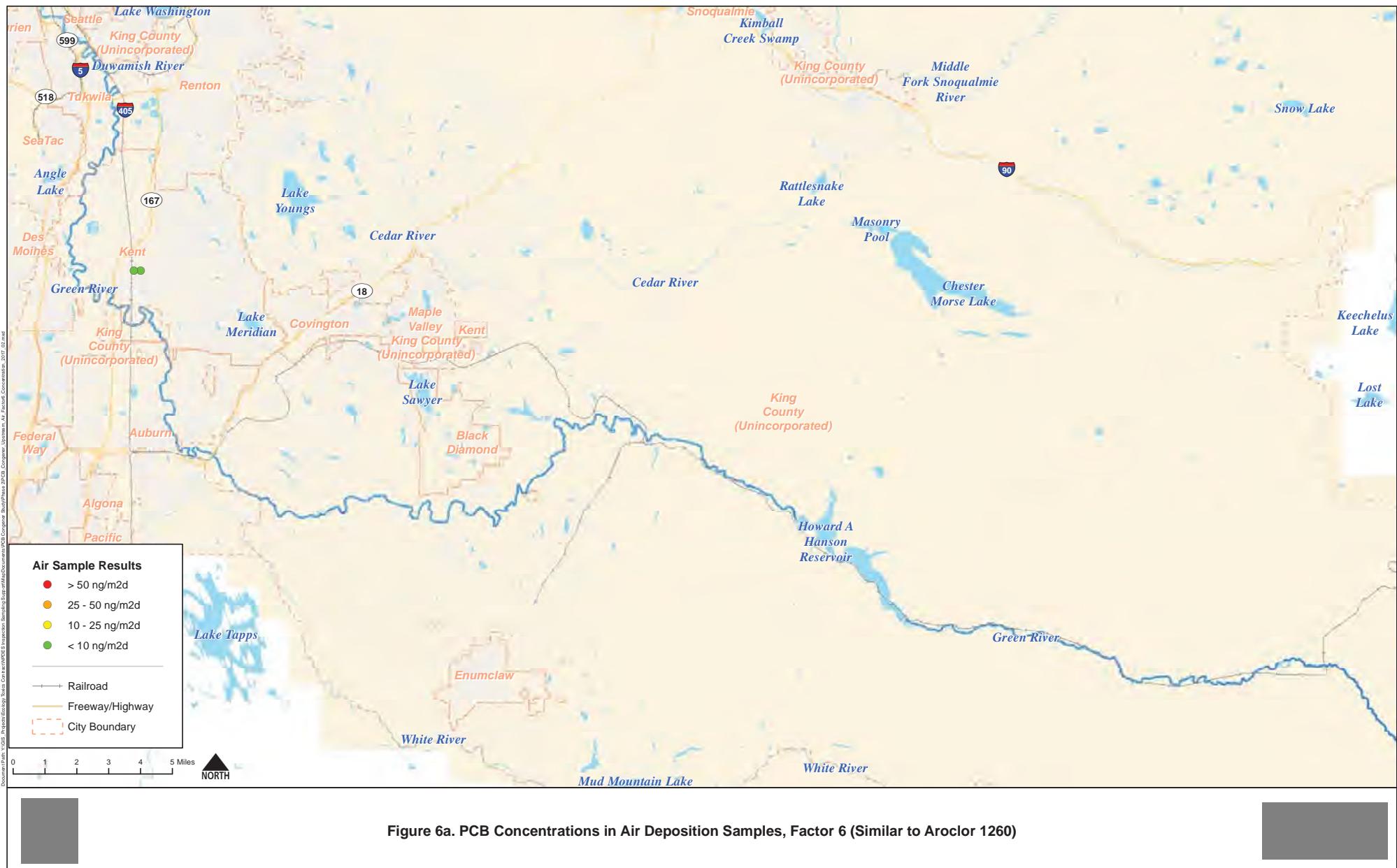




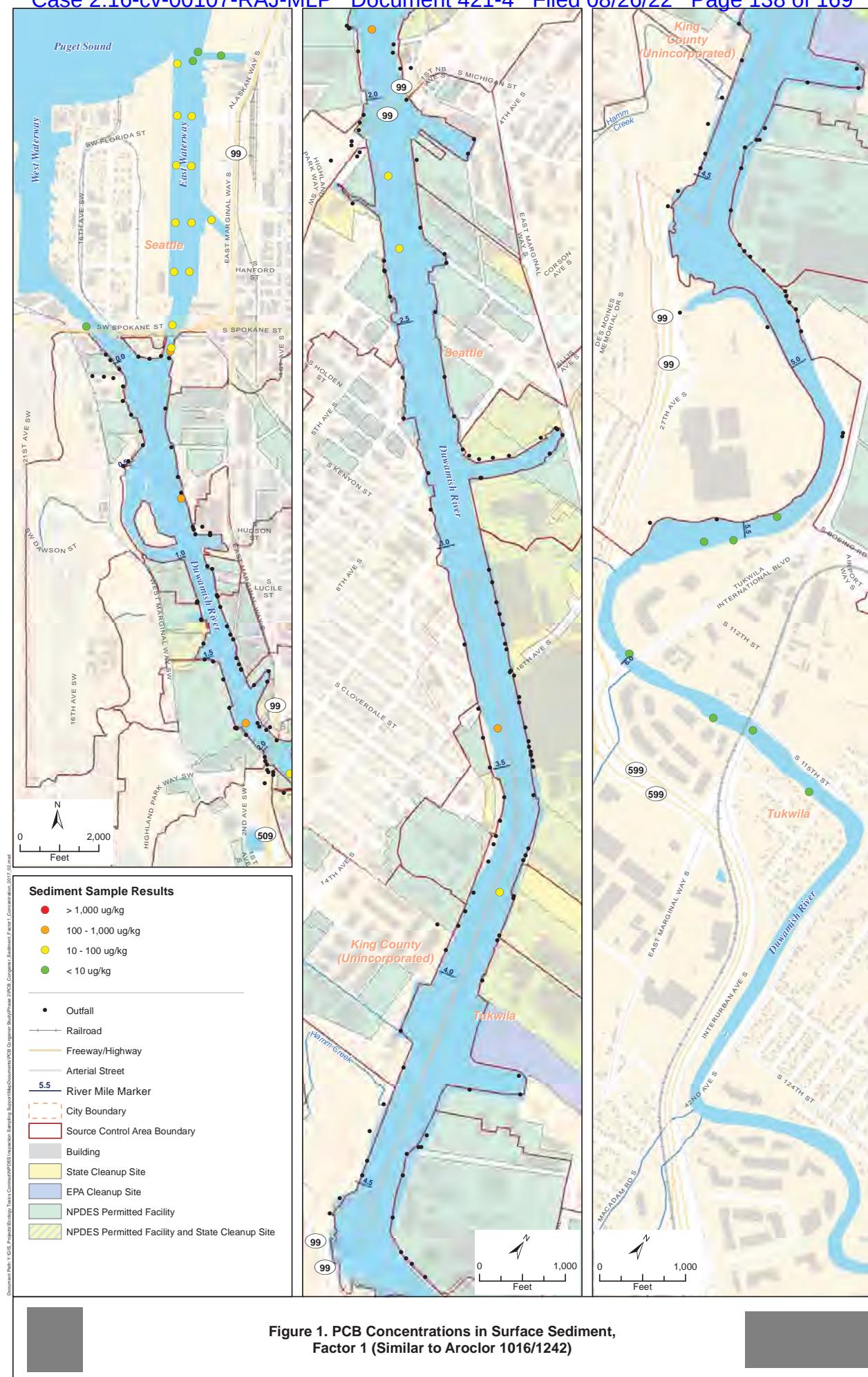


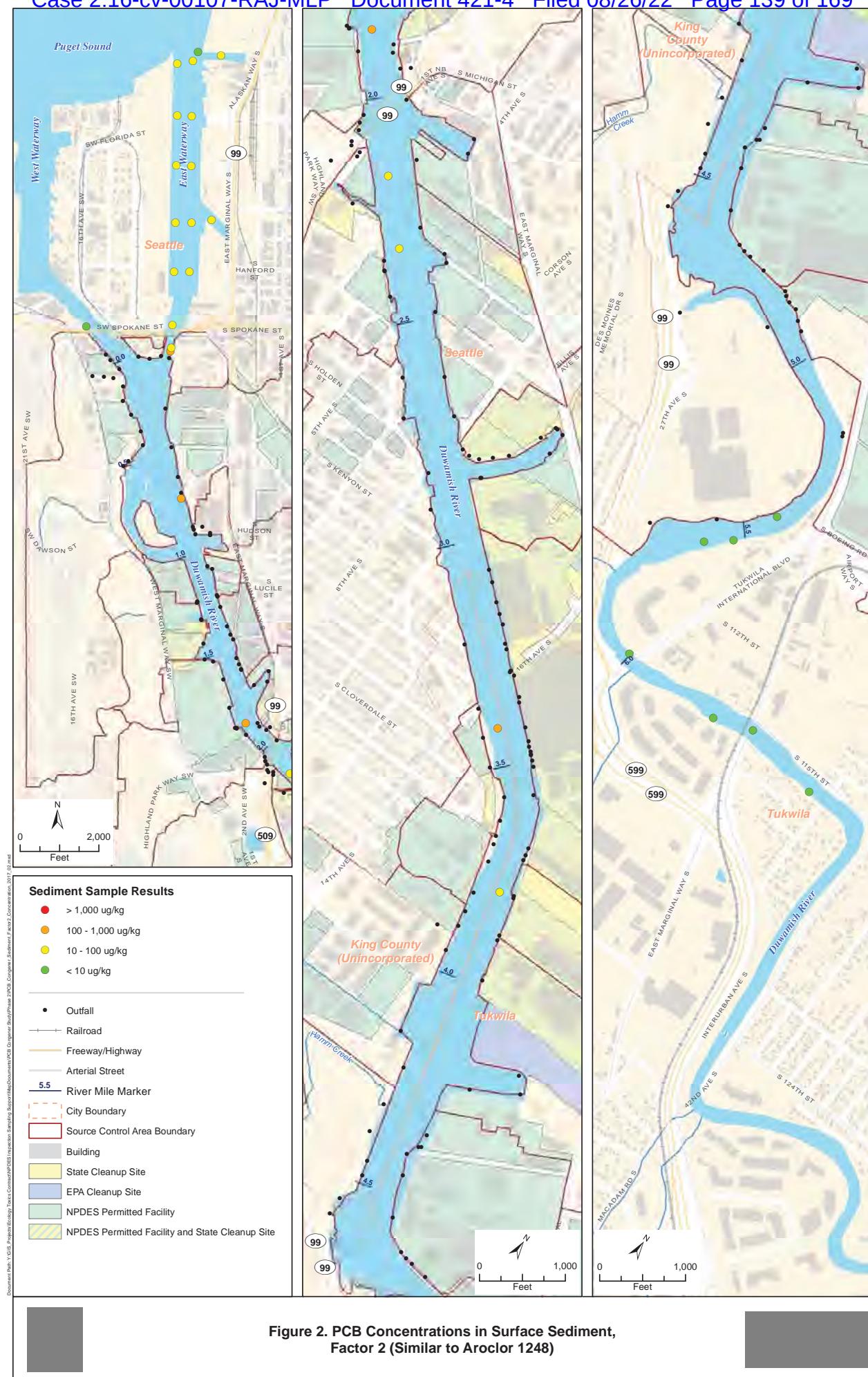


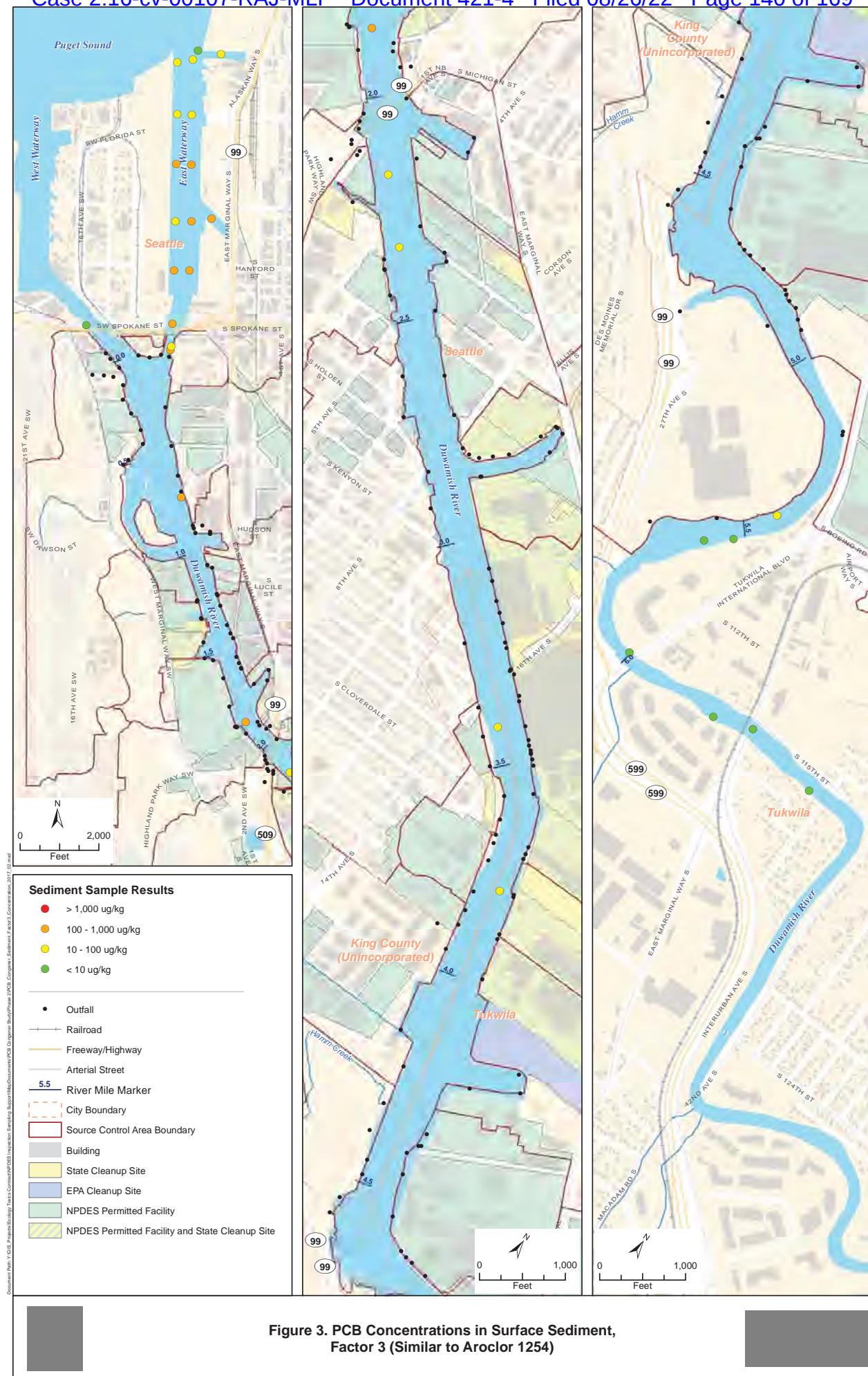


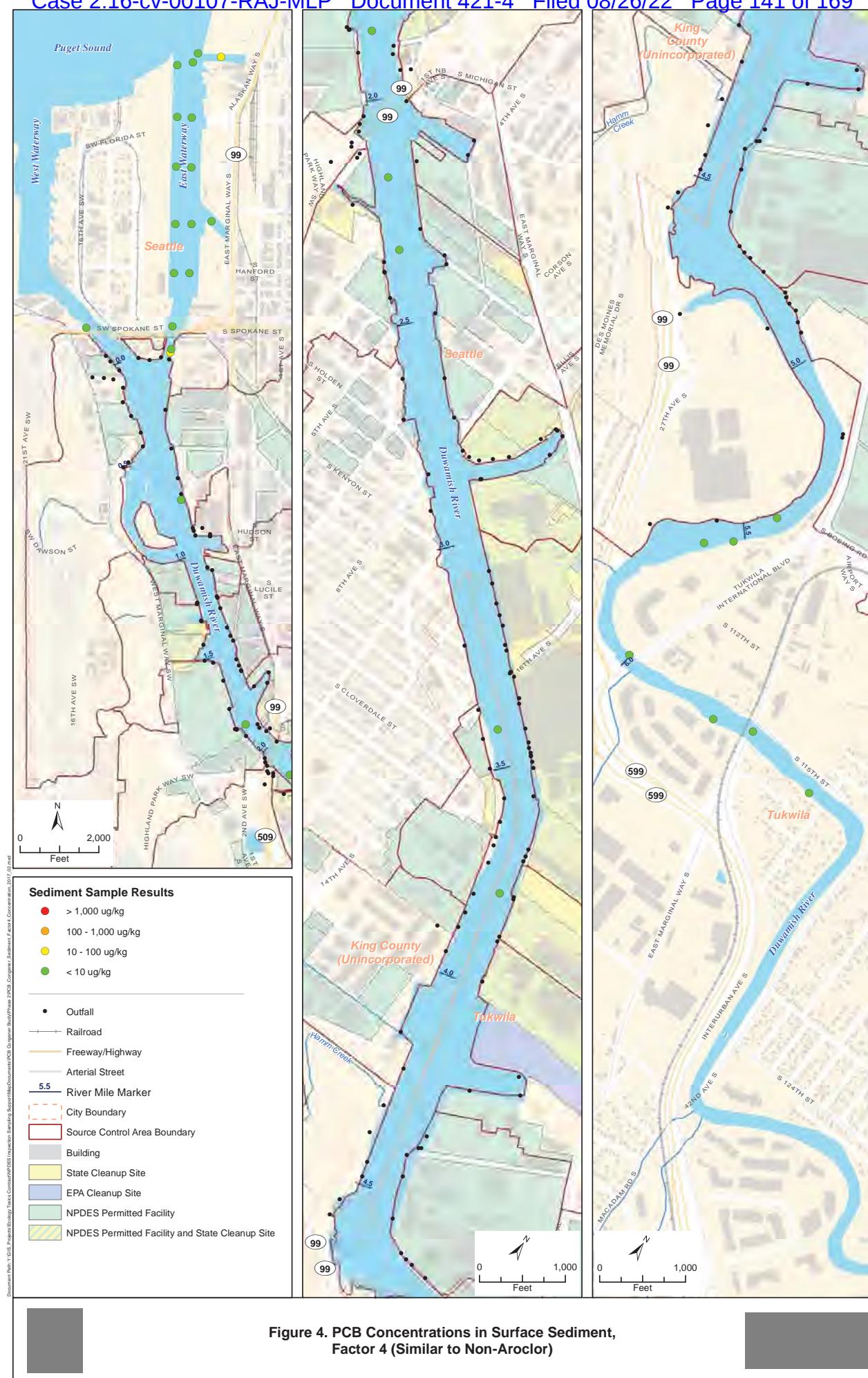


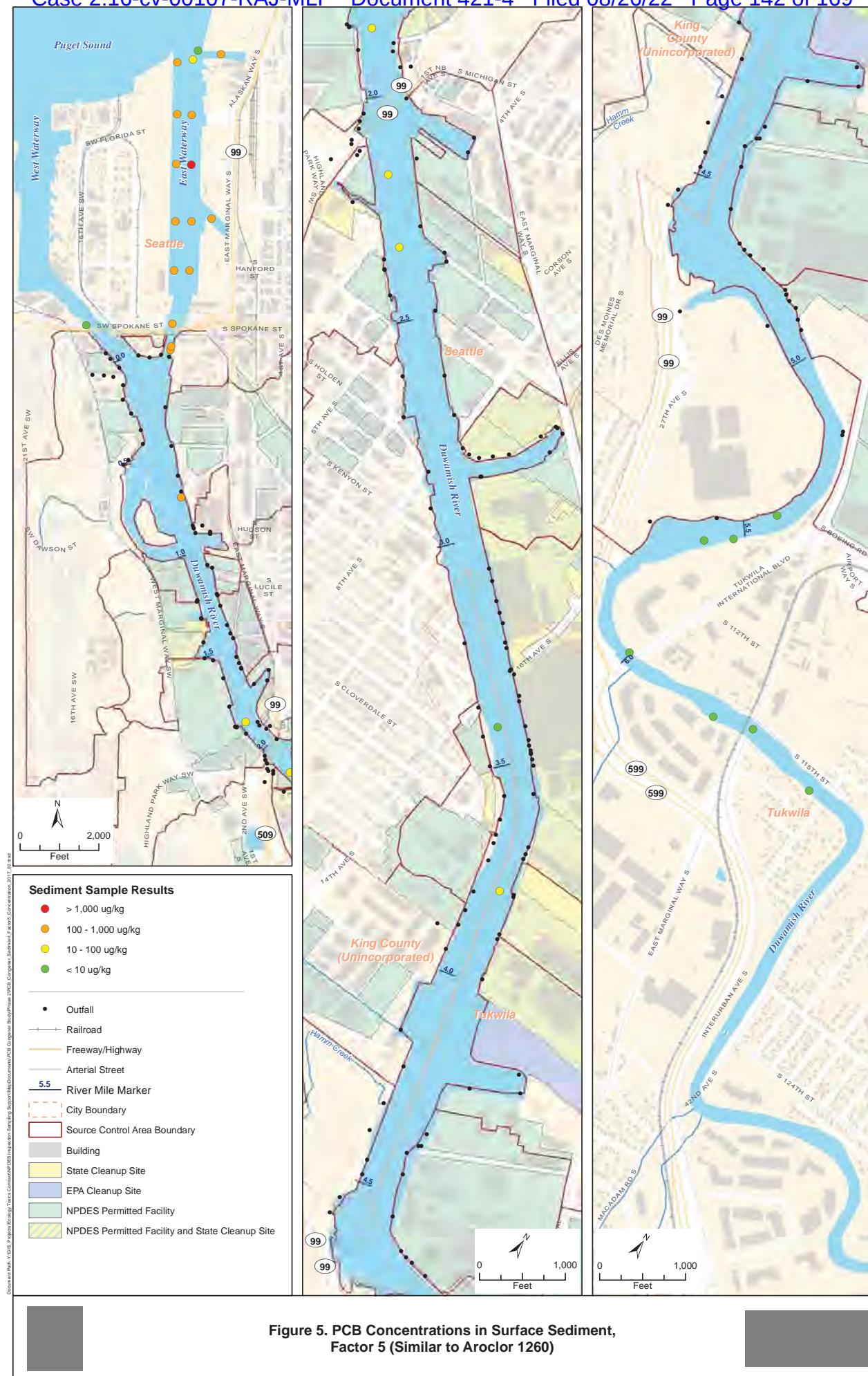
PCB Concentrations in Sediment Samples

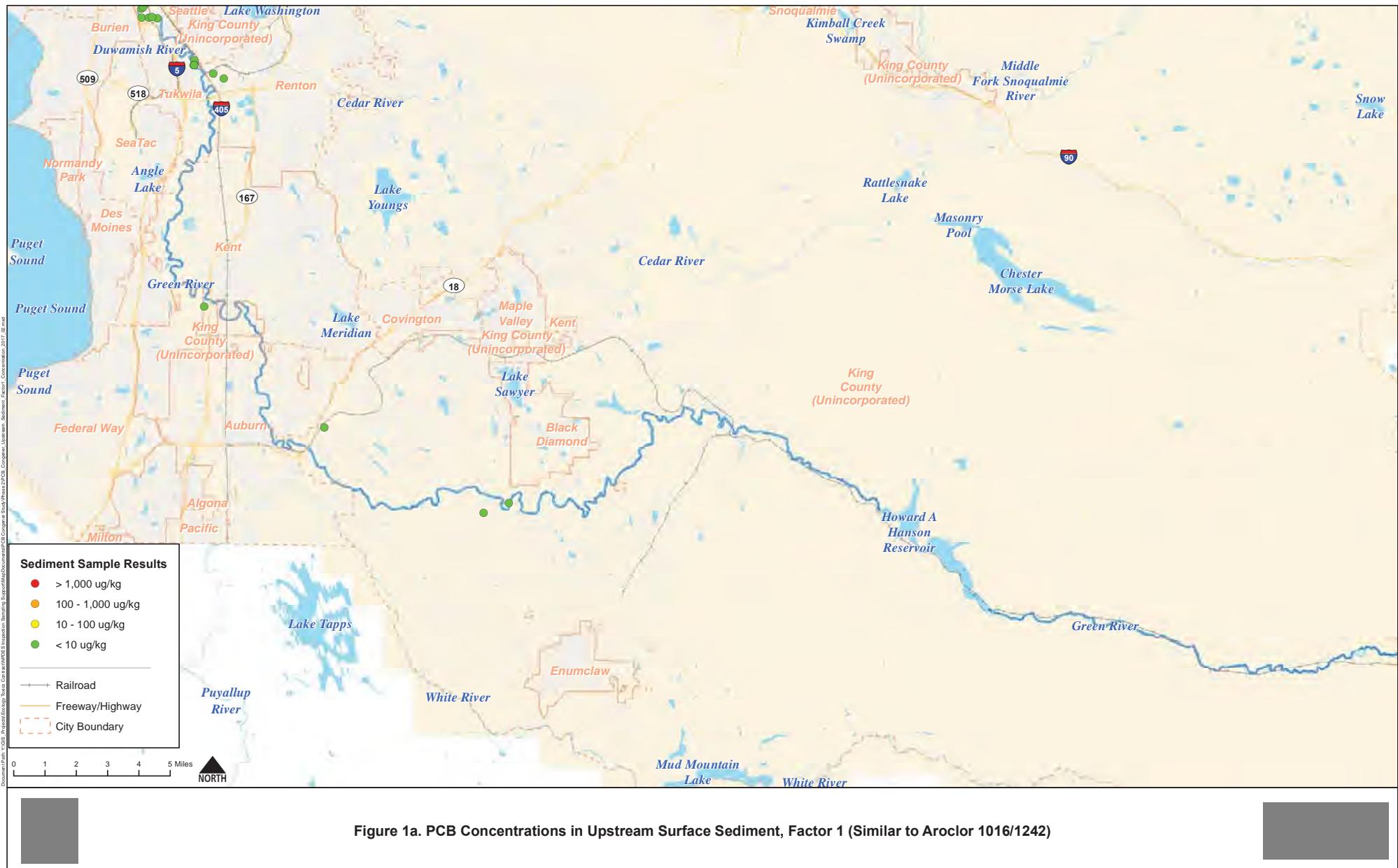


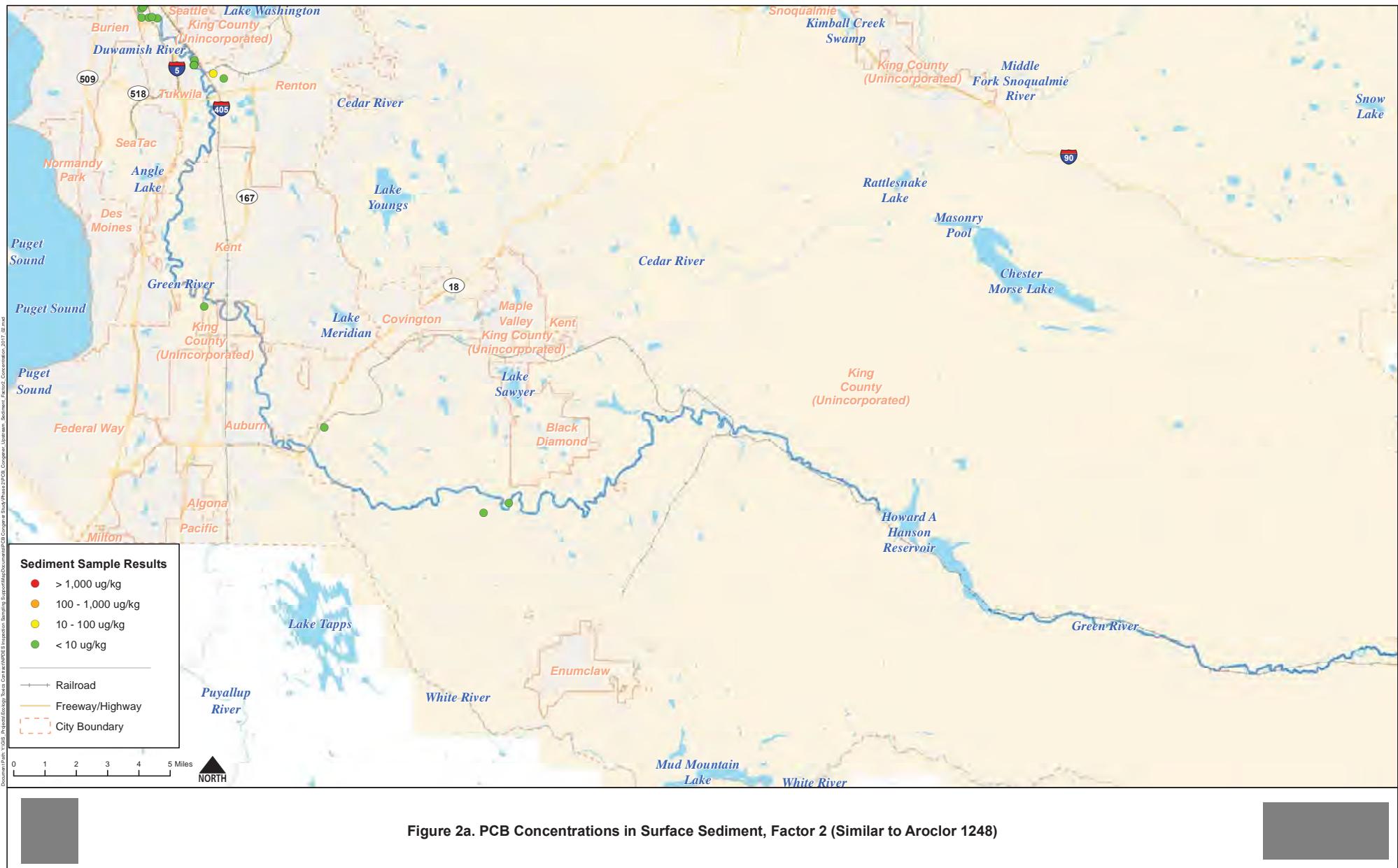


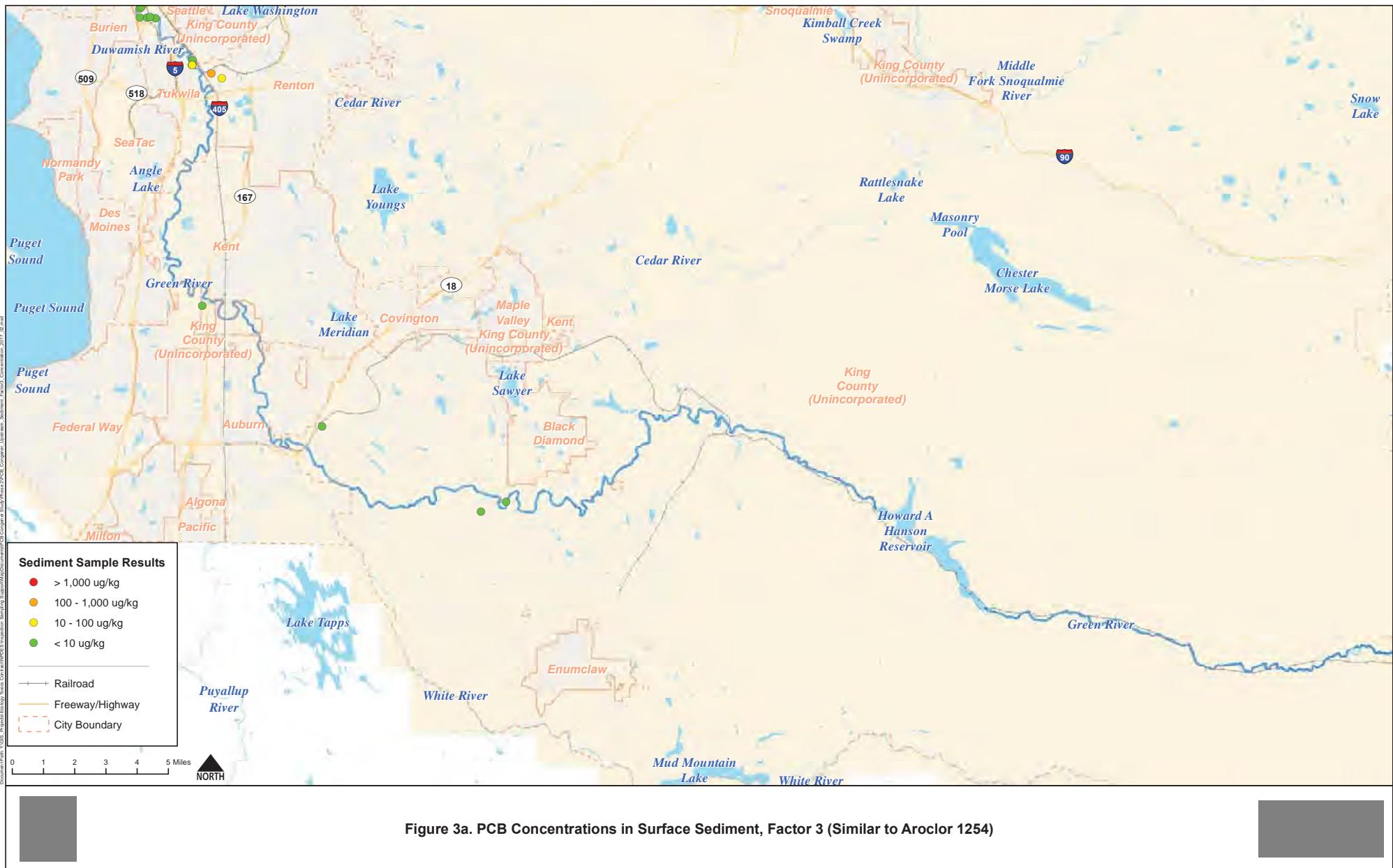


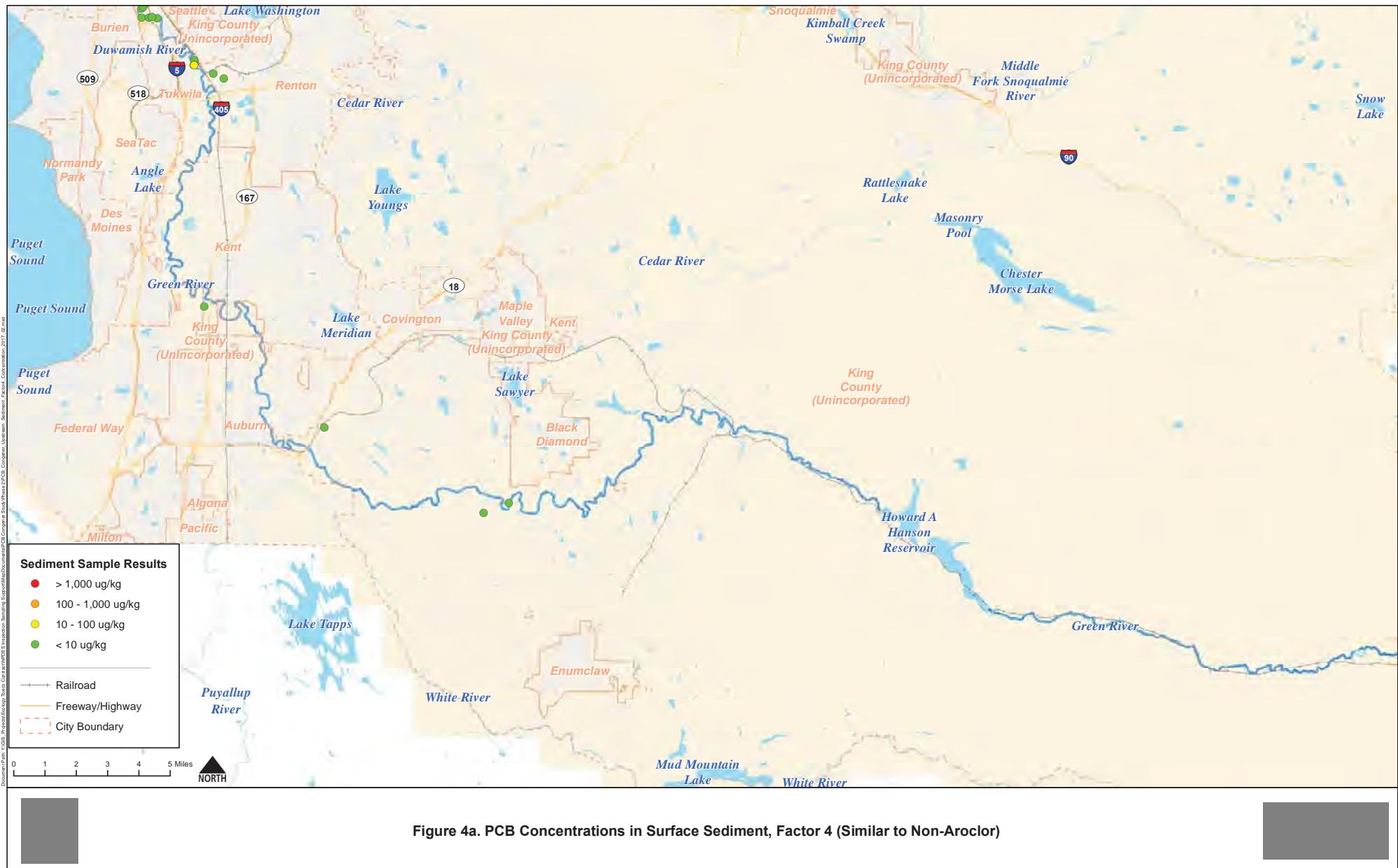


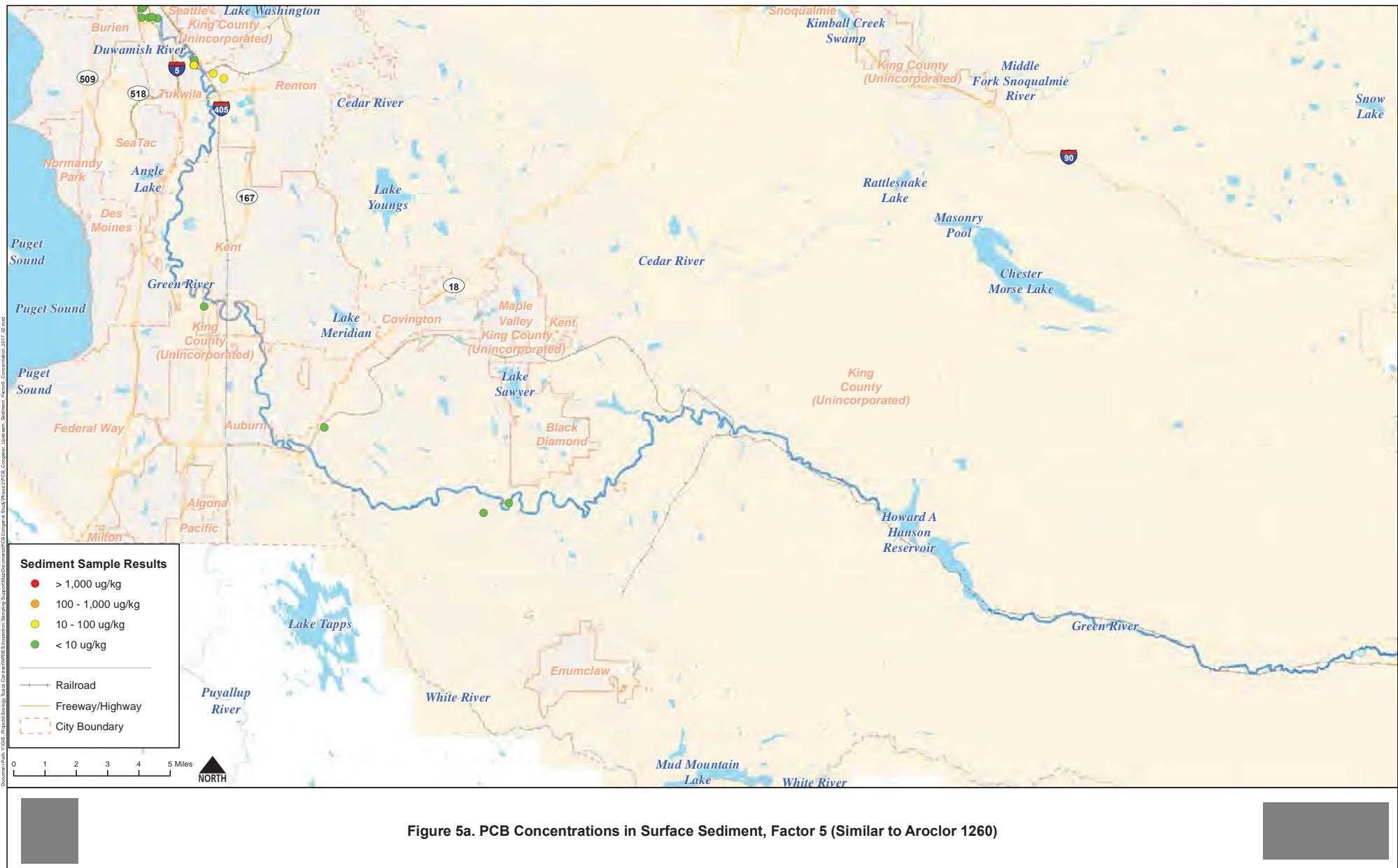






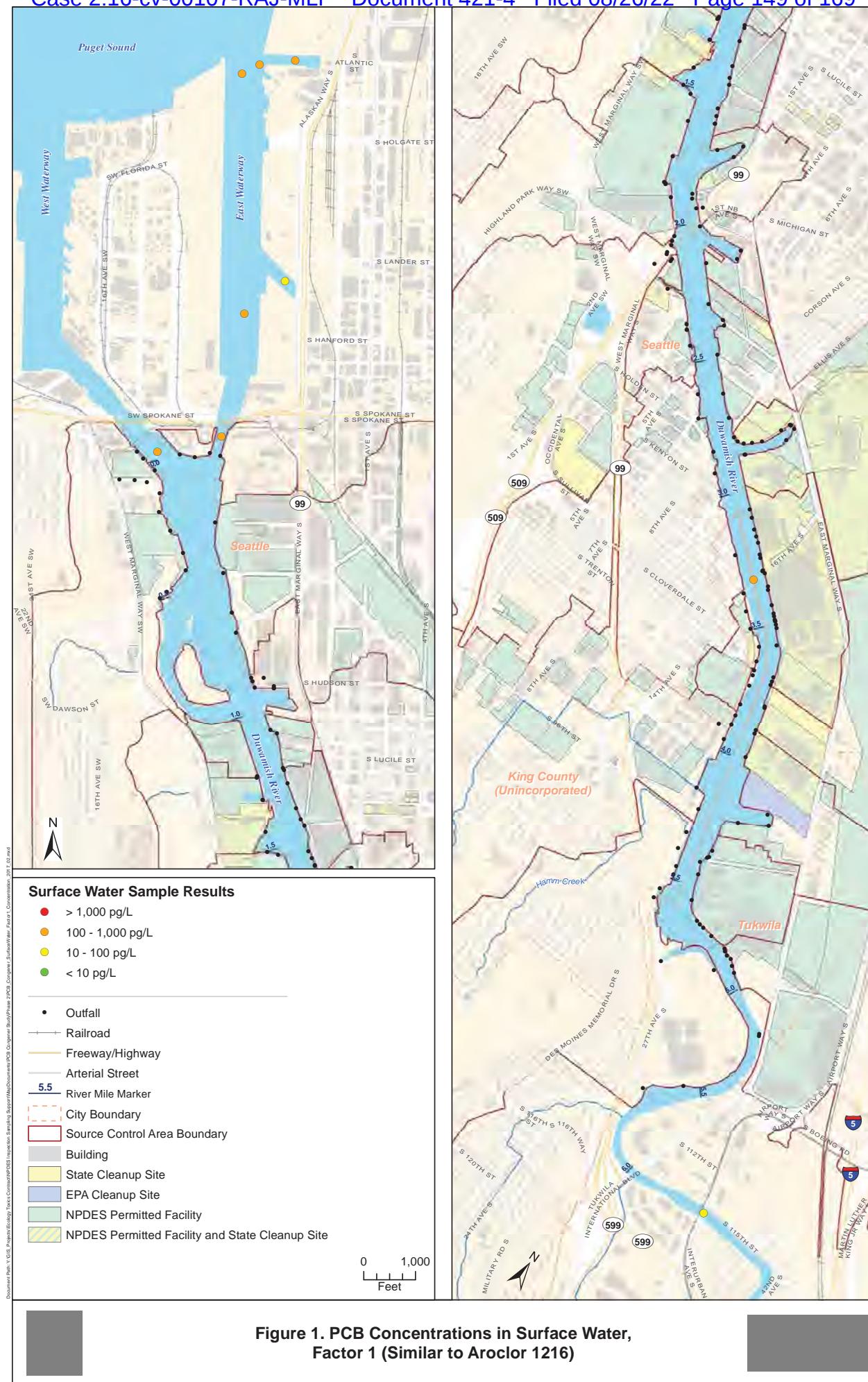


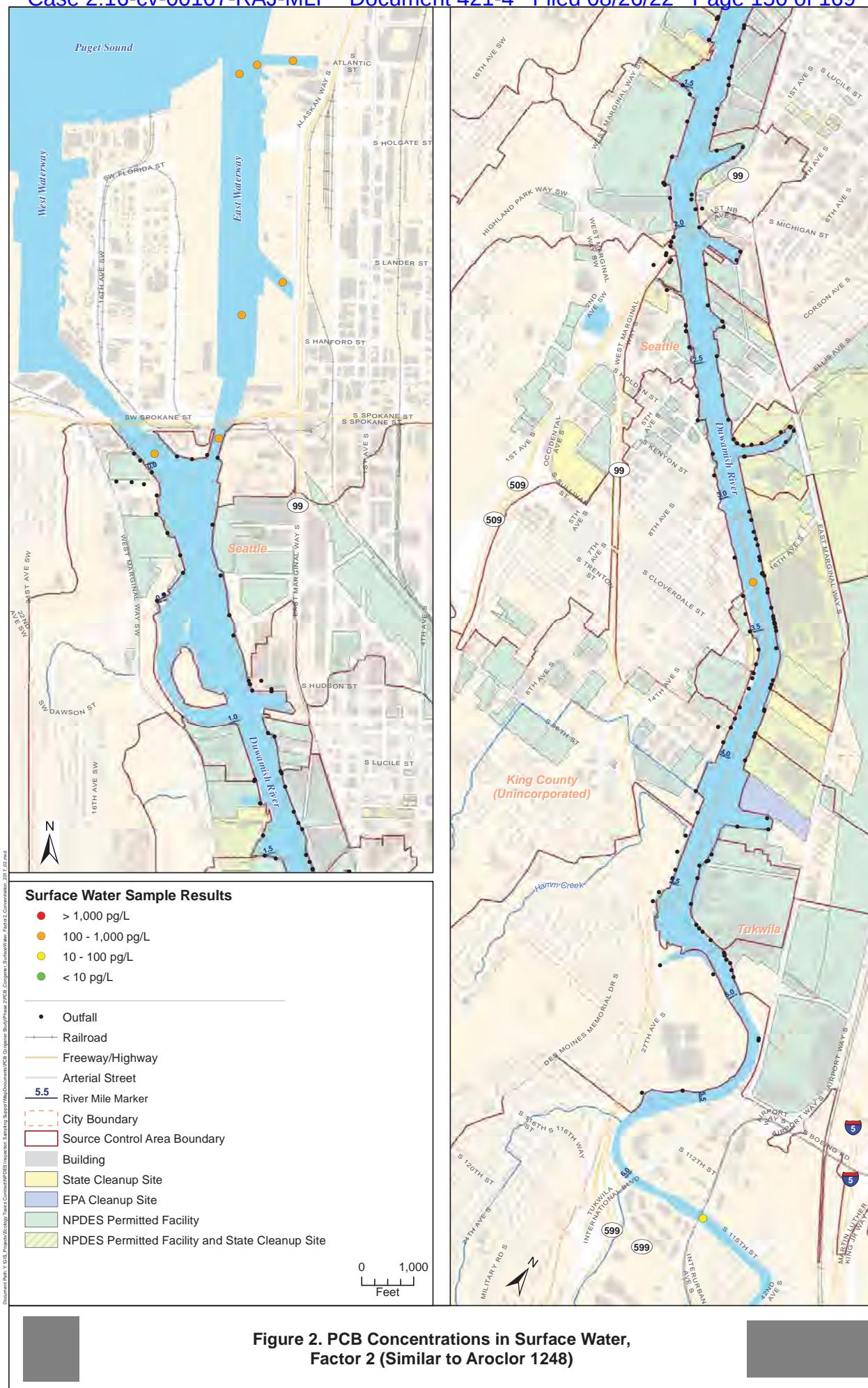


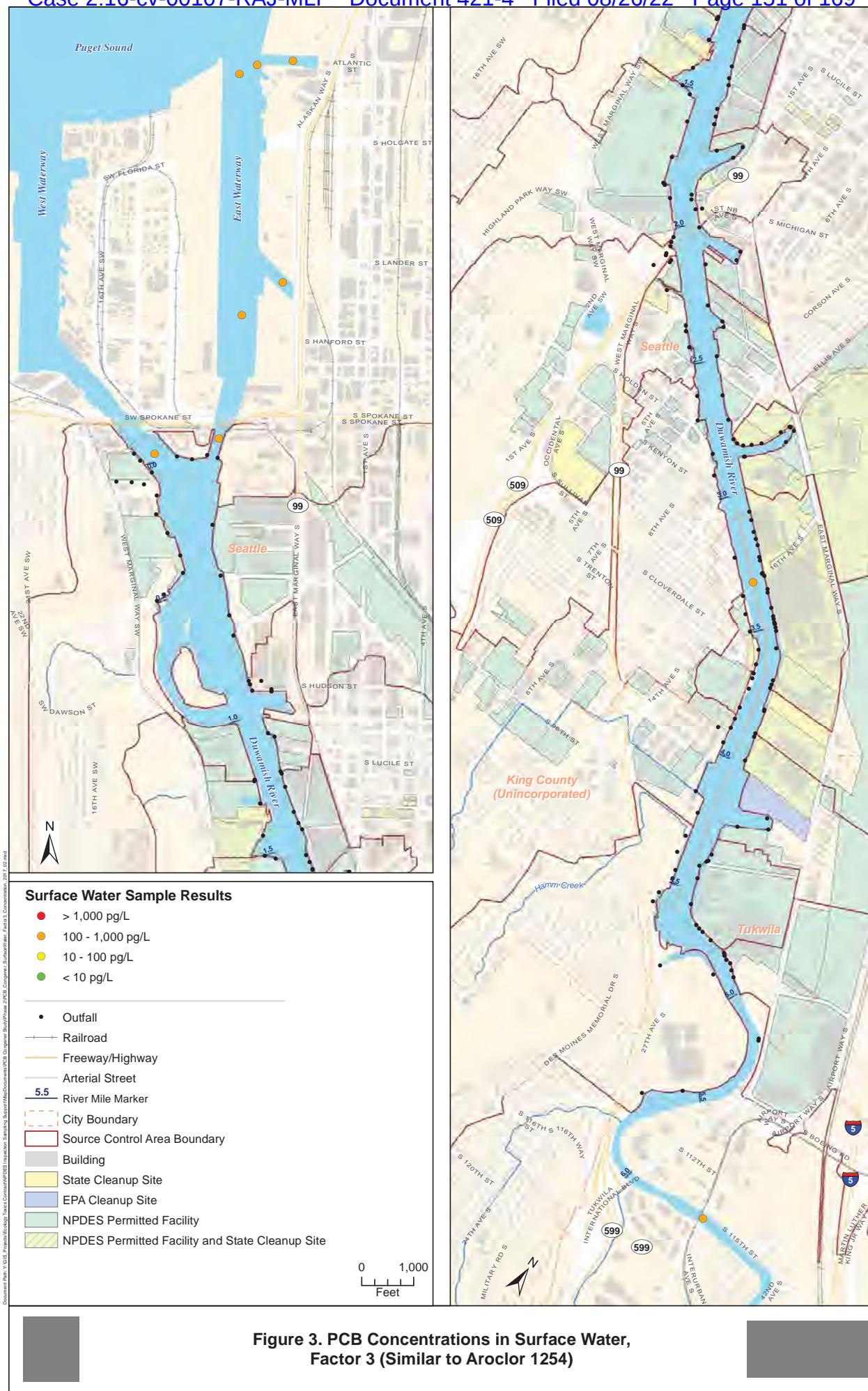


PCB Congener Study Phase 2 - Source Evaluation

PCB Concentrations in Surface Water Samples







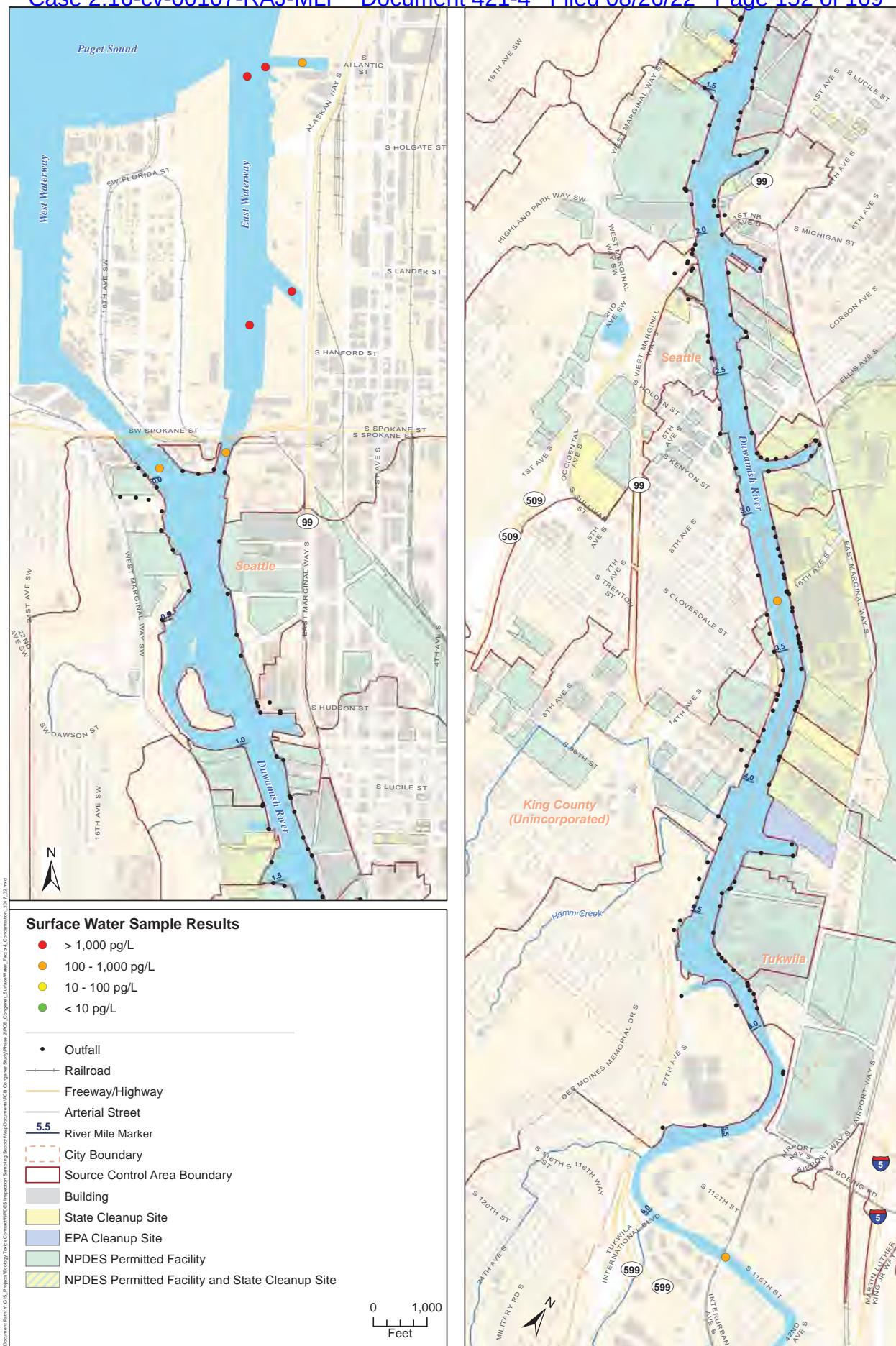
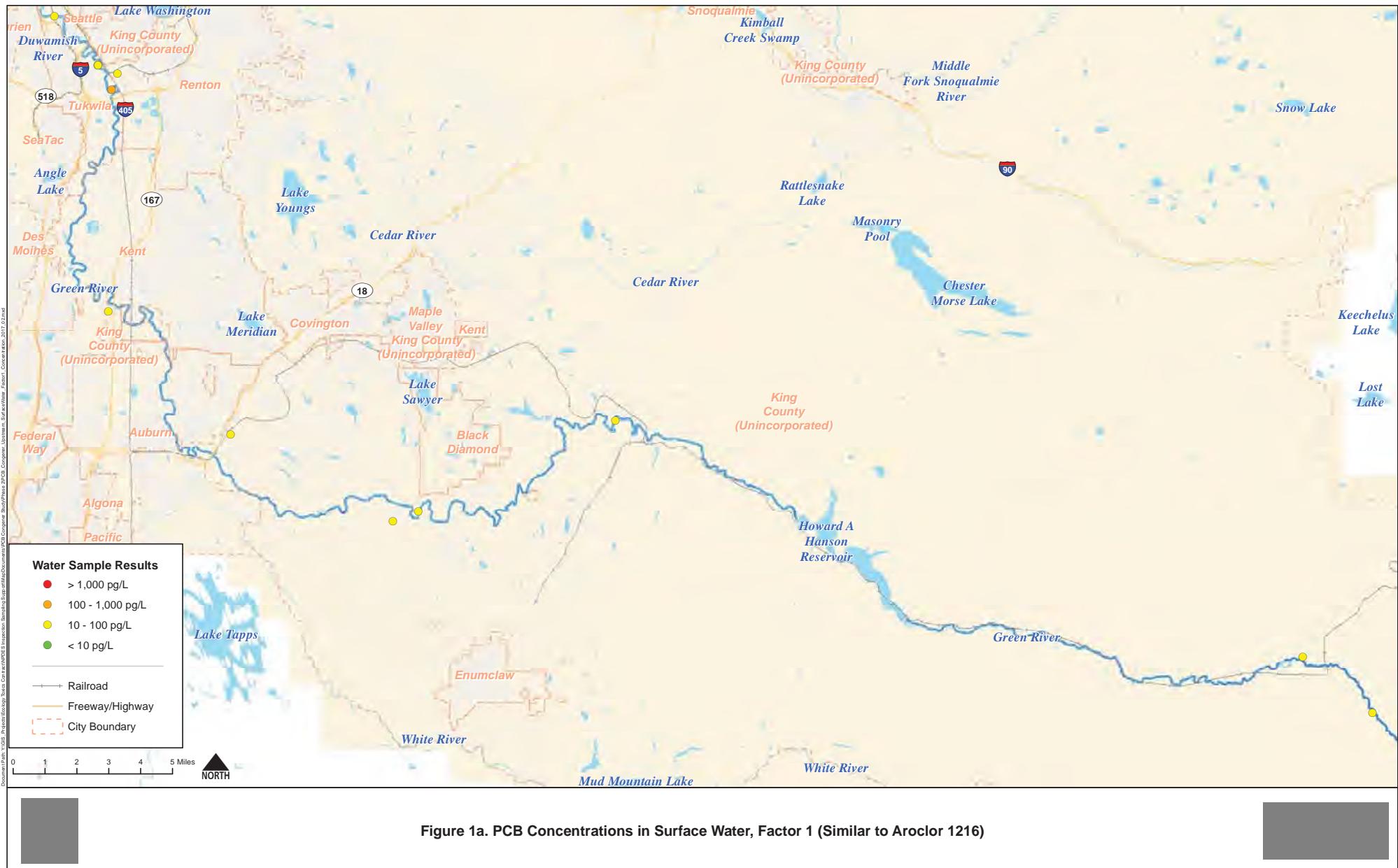
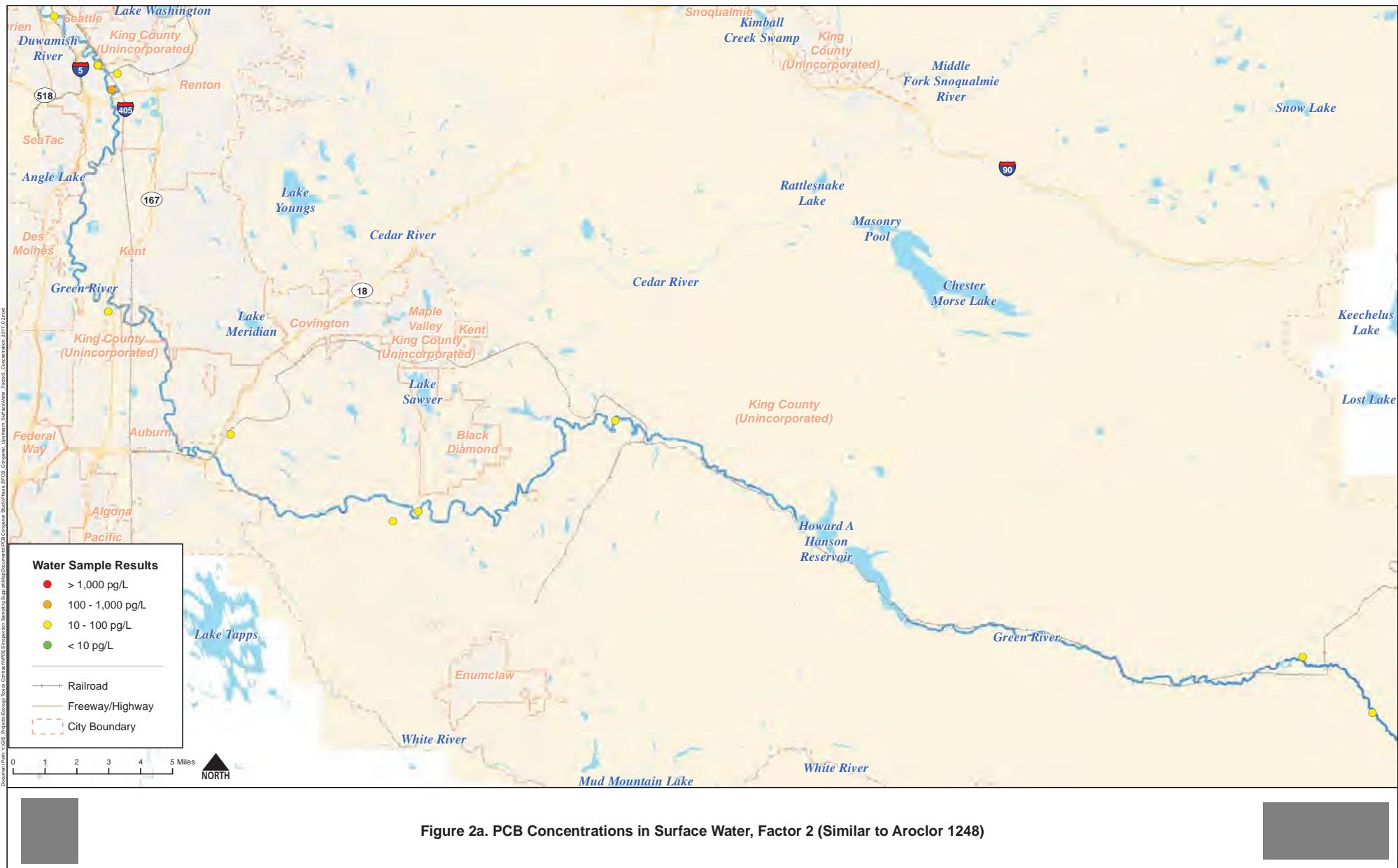
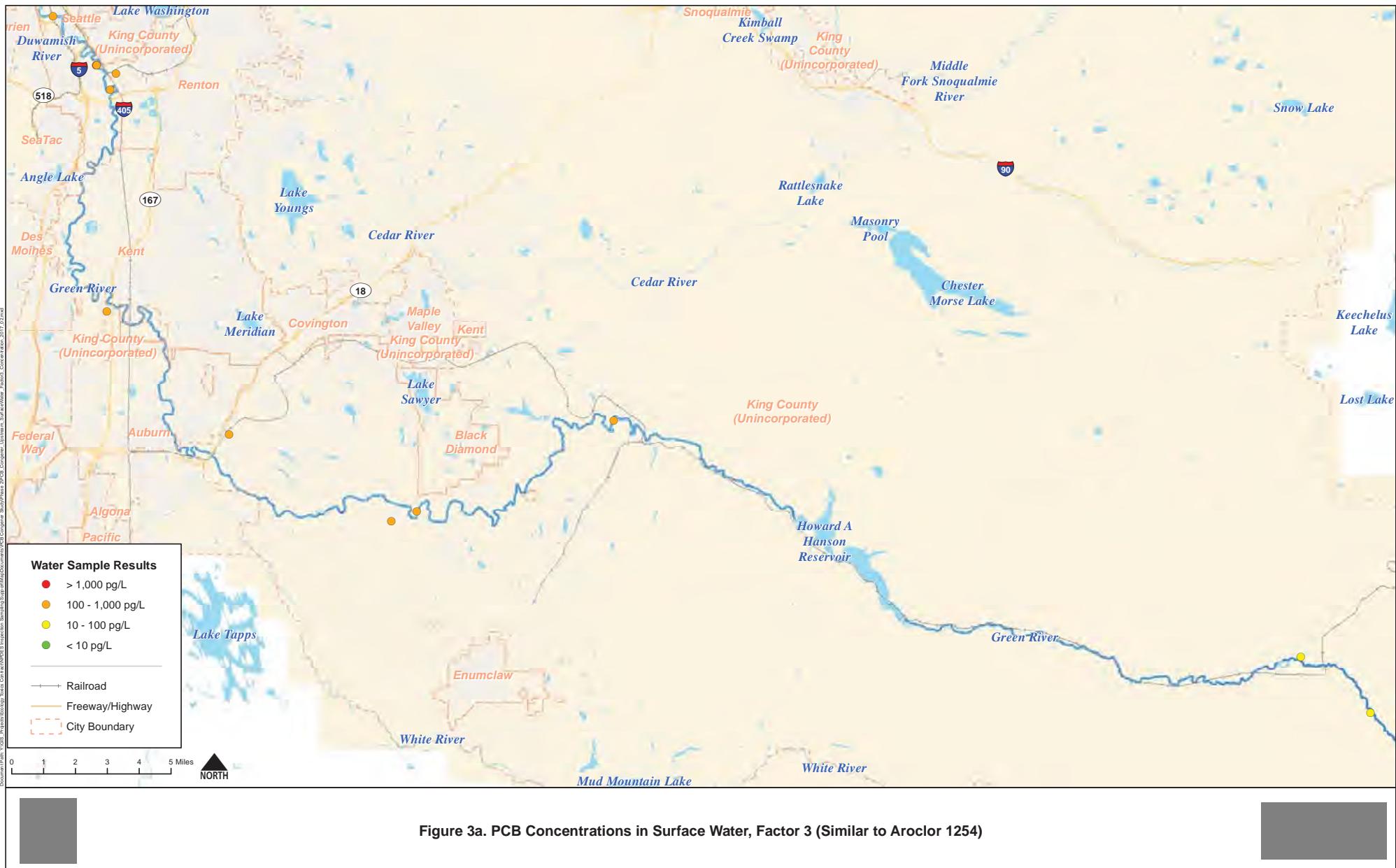
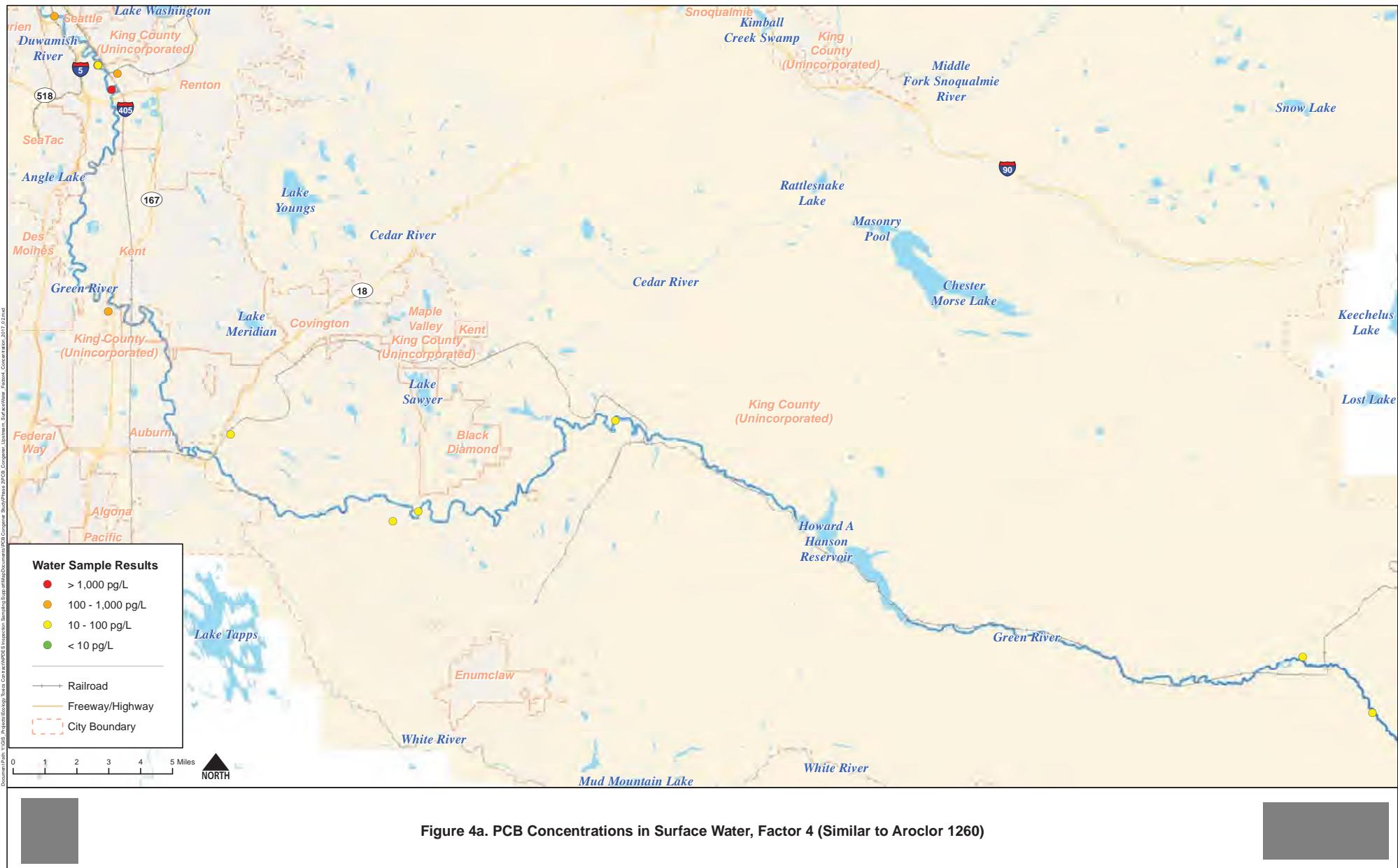


Figure 4. PCB Concentrations in Surface Water, Factor 4 (Similar to Aroclor 1260)

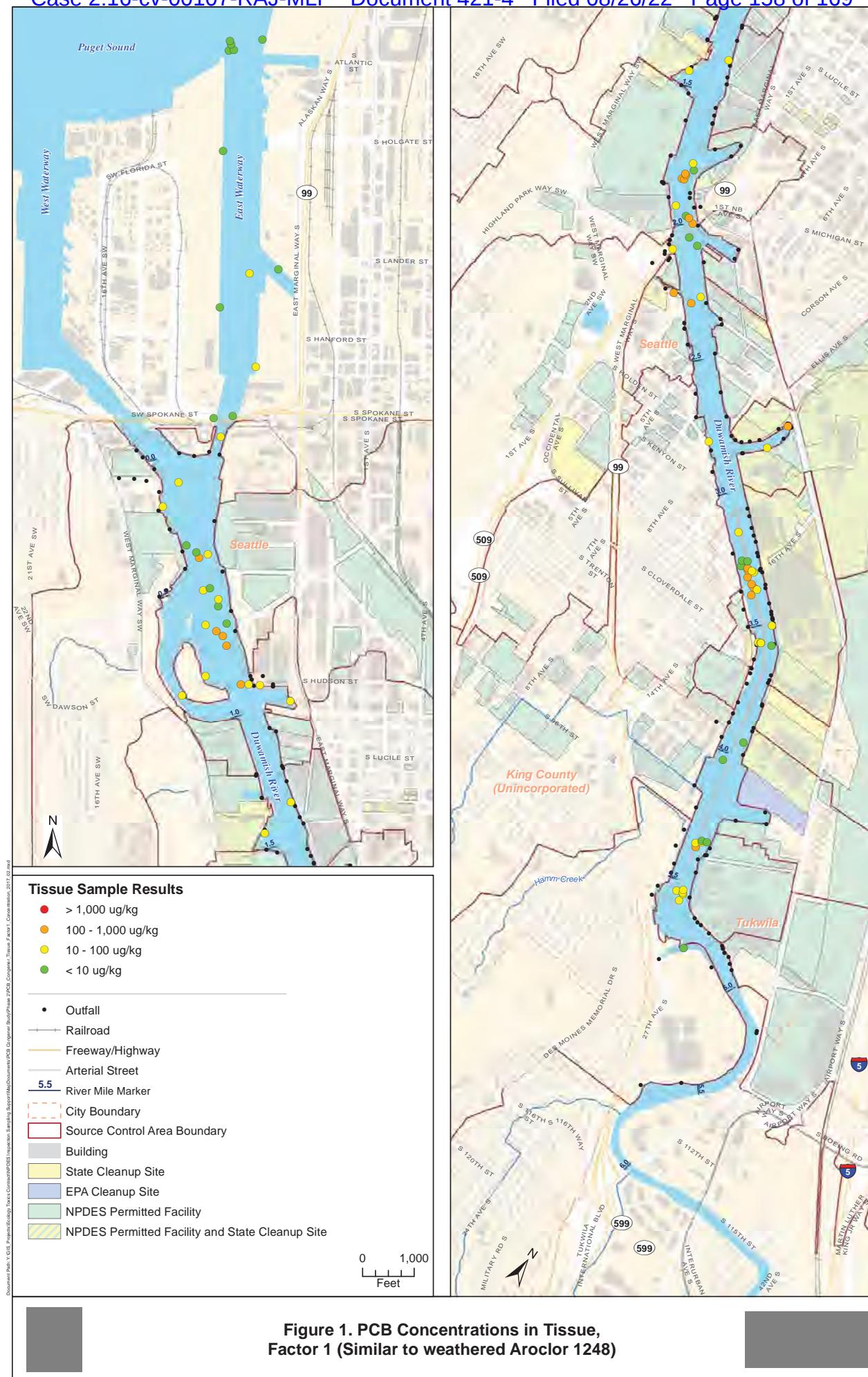


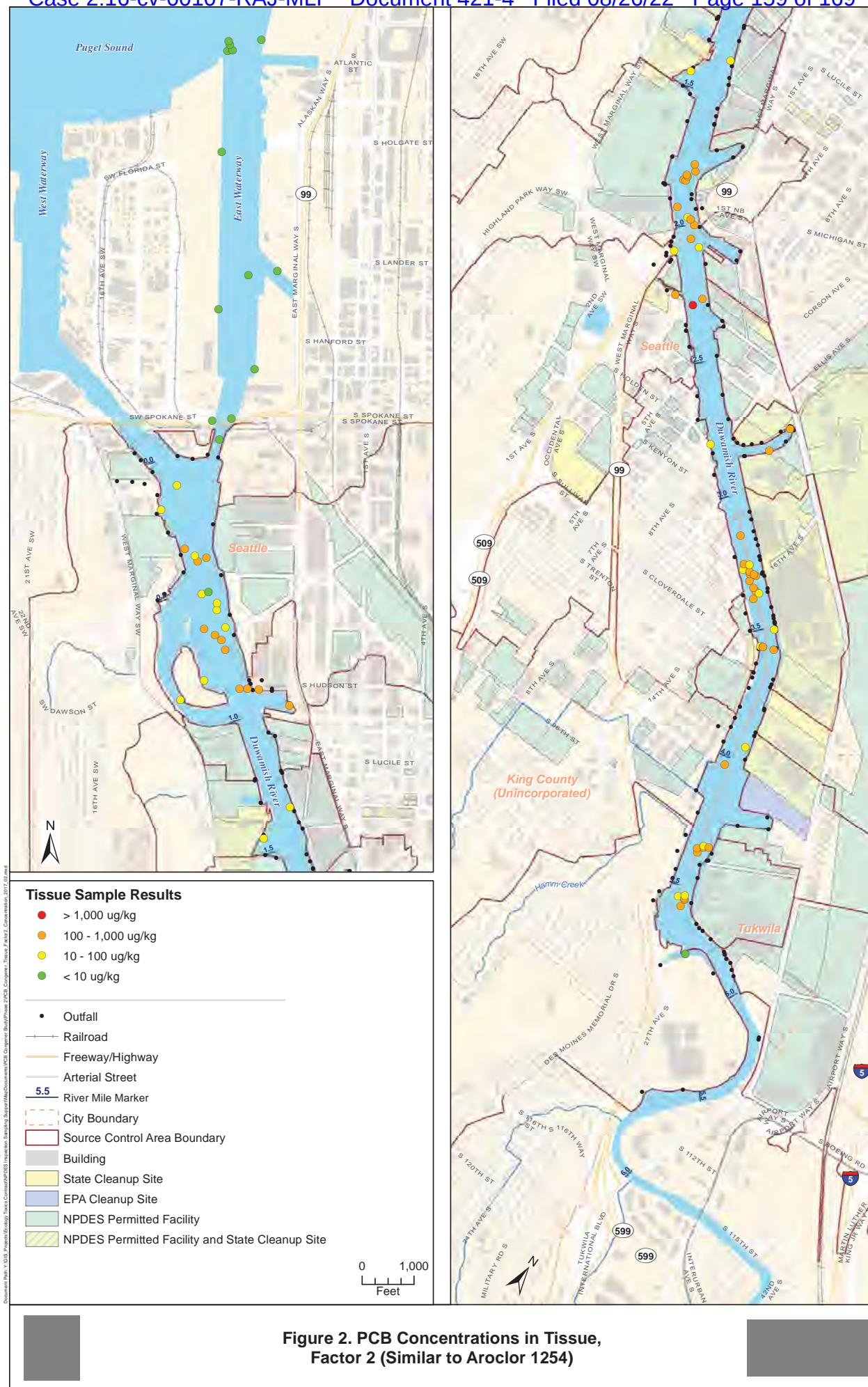


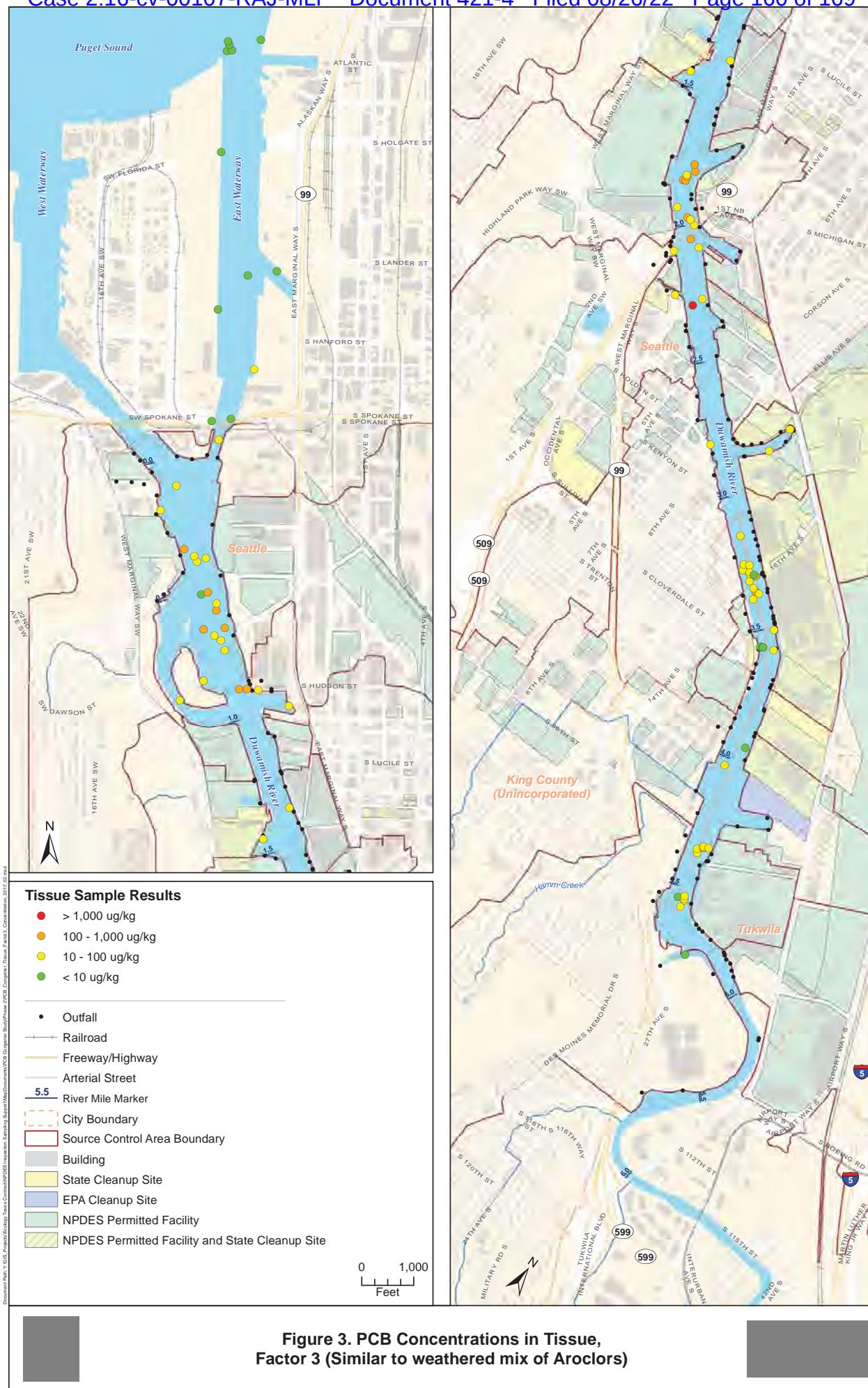


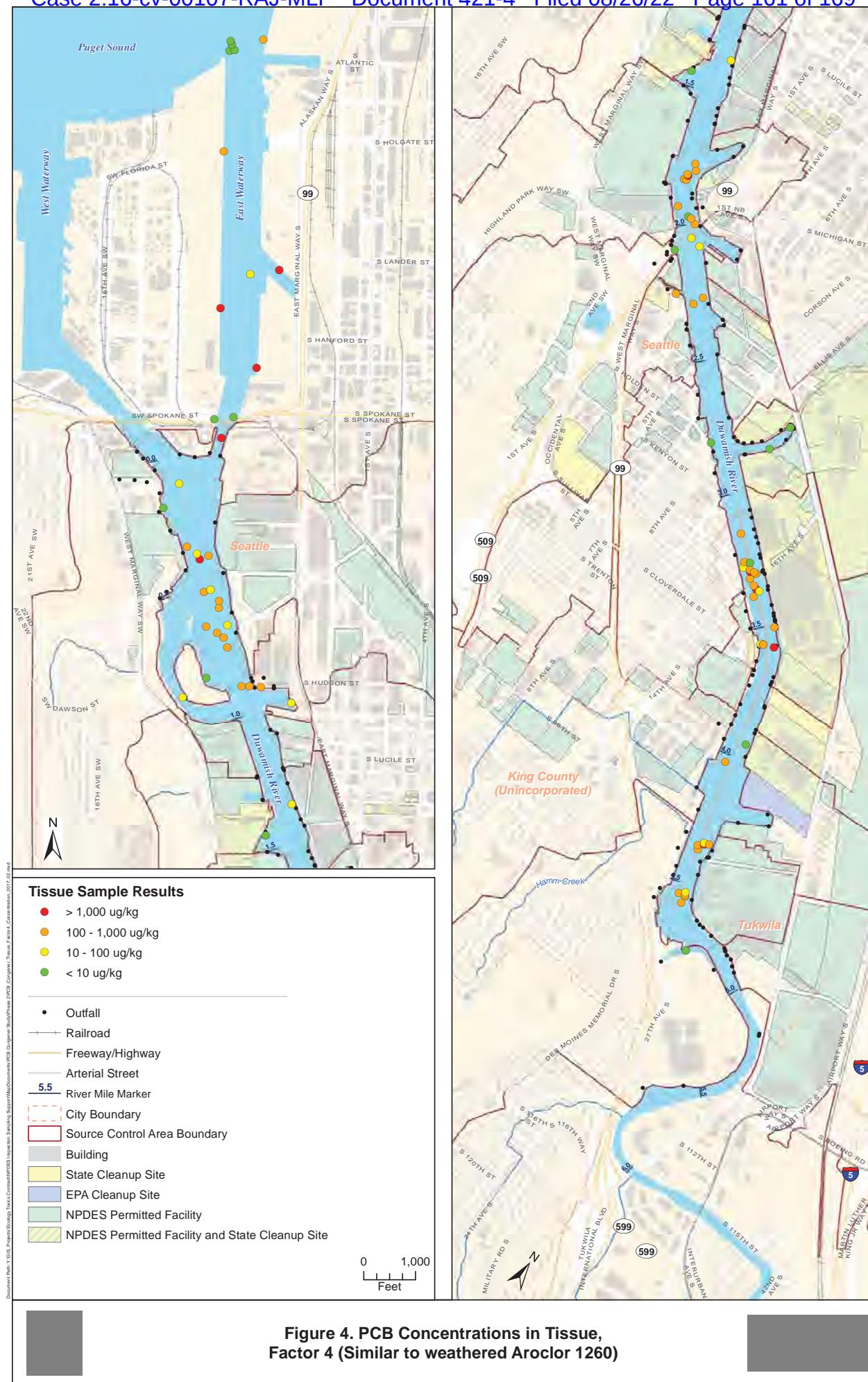


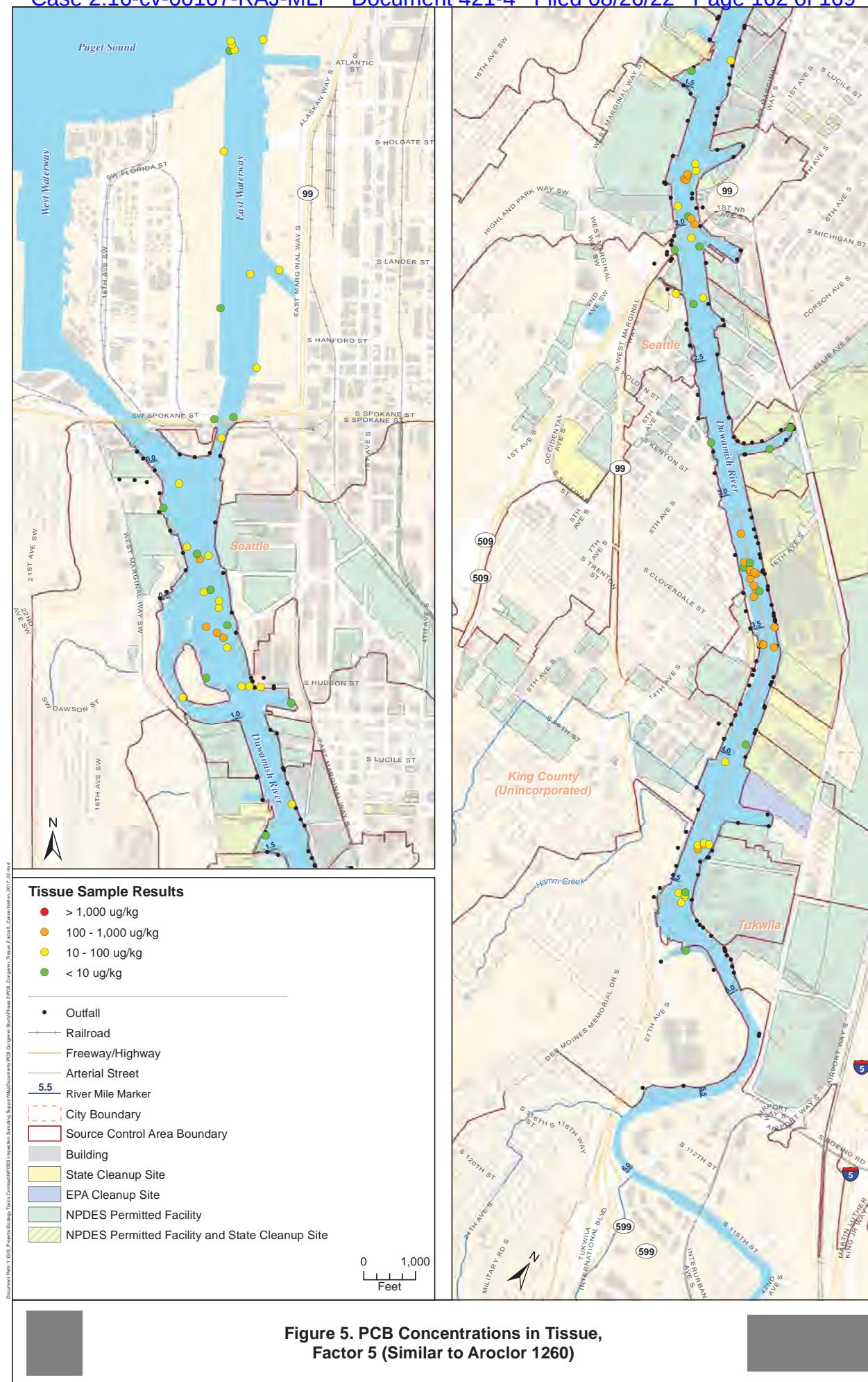
PCB Concentrations in Tissue Samples





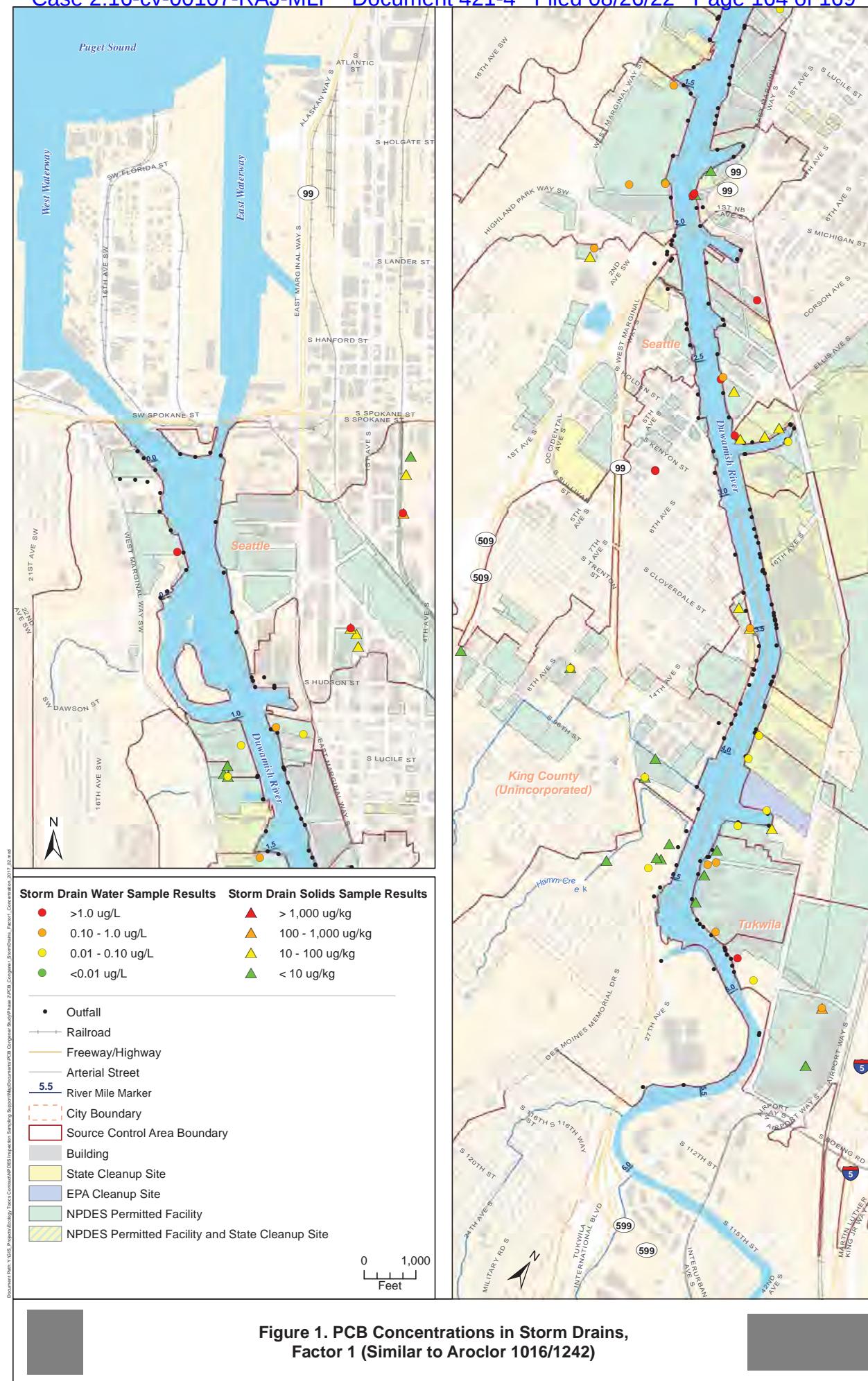


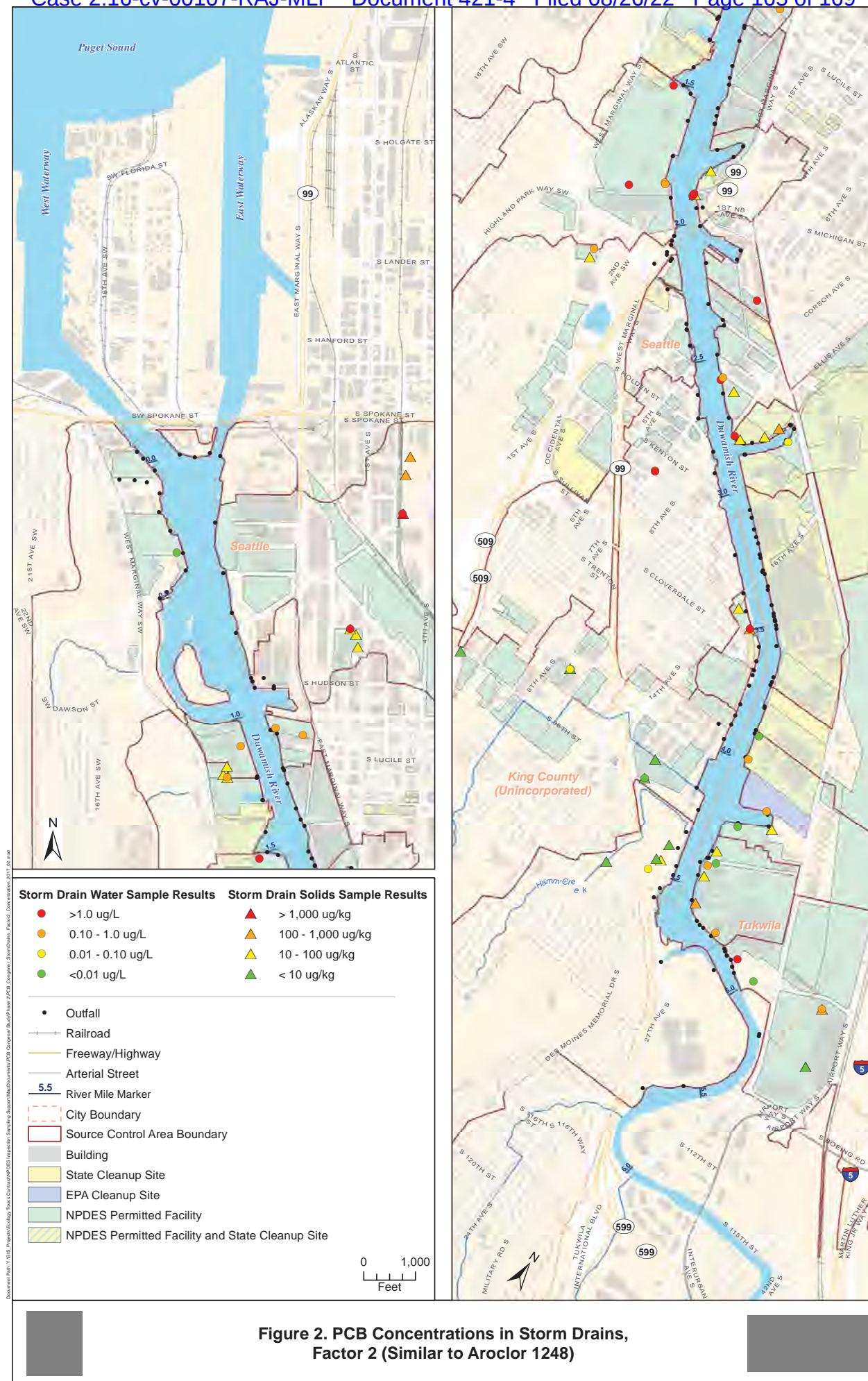


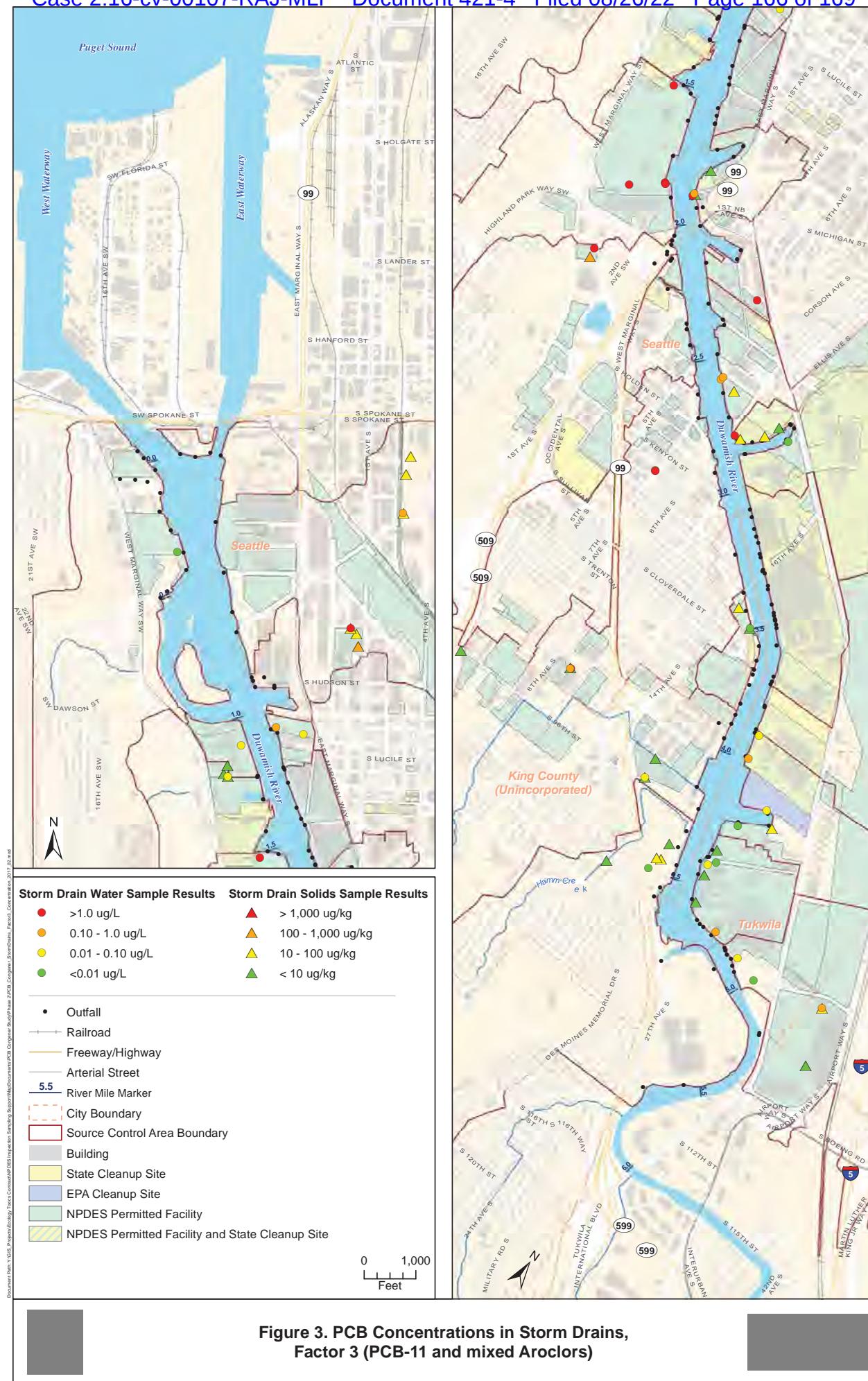


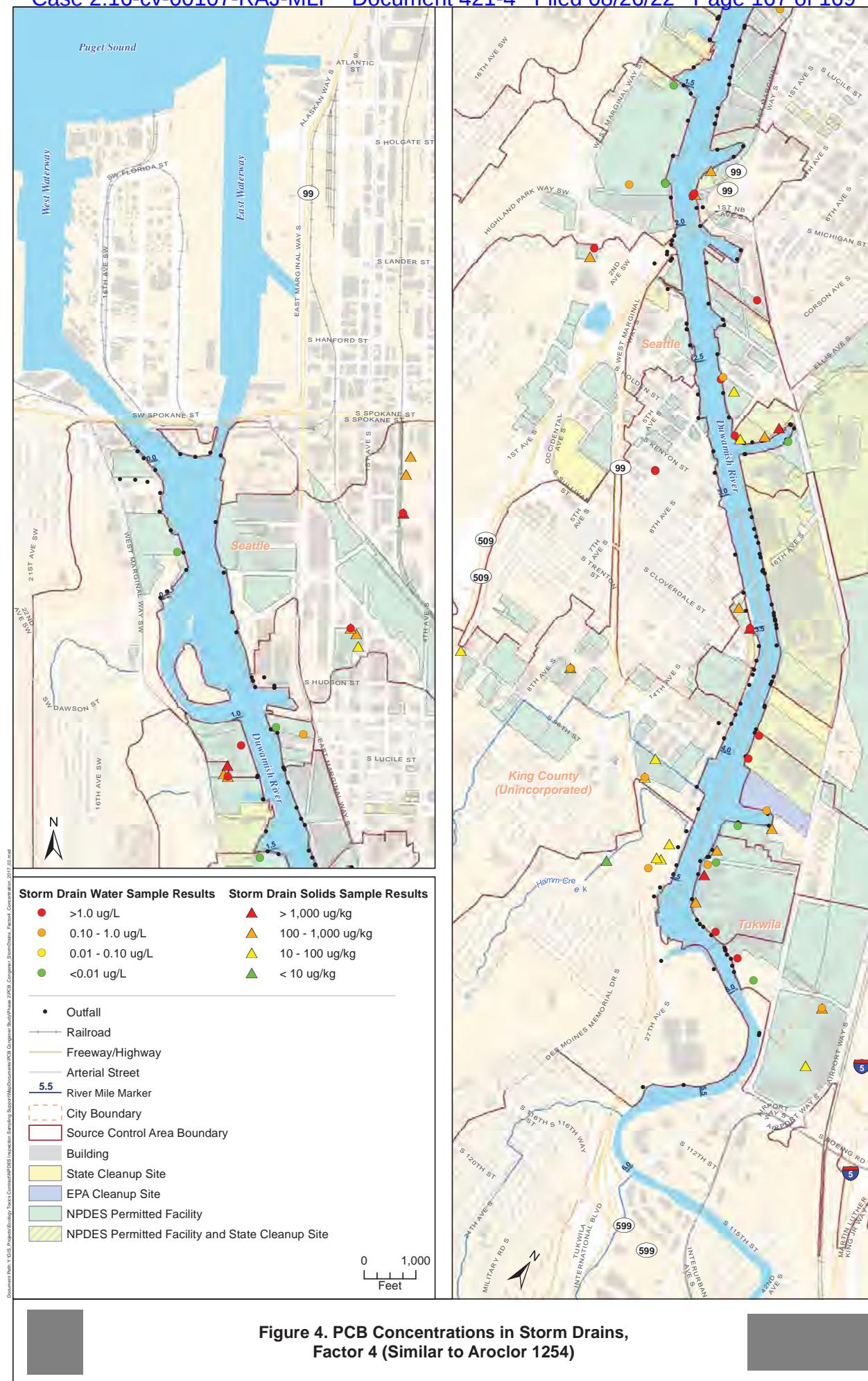
PCB Congener Study Phase 2 - Source Evaluation

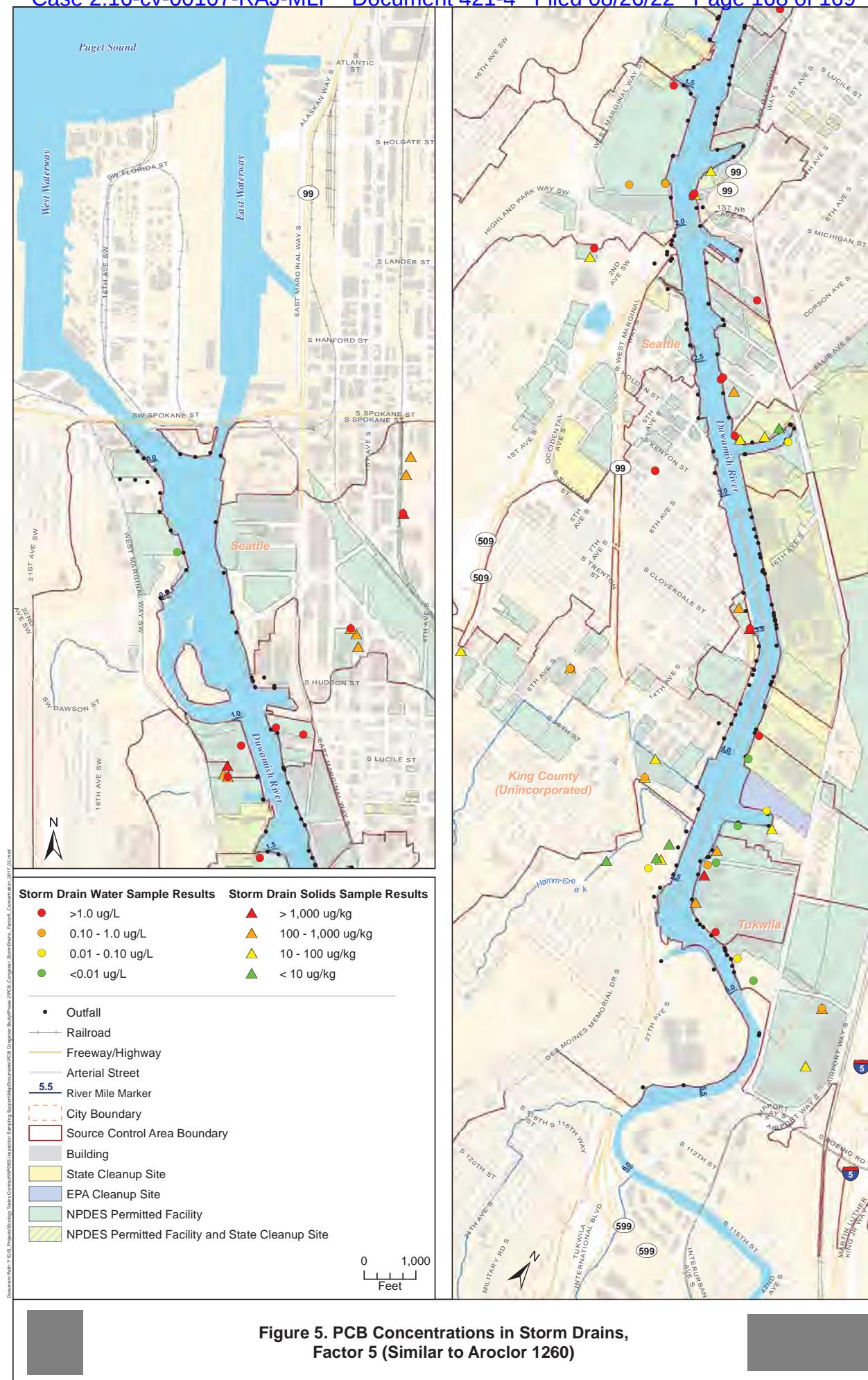
PCB Concentrations in Storm Drain Samples











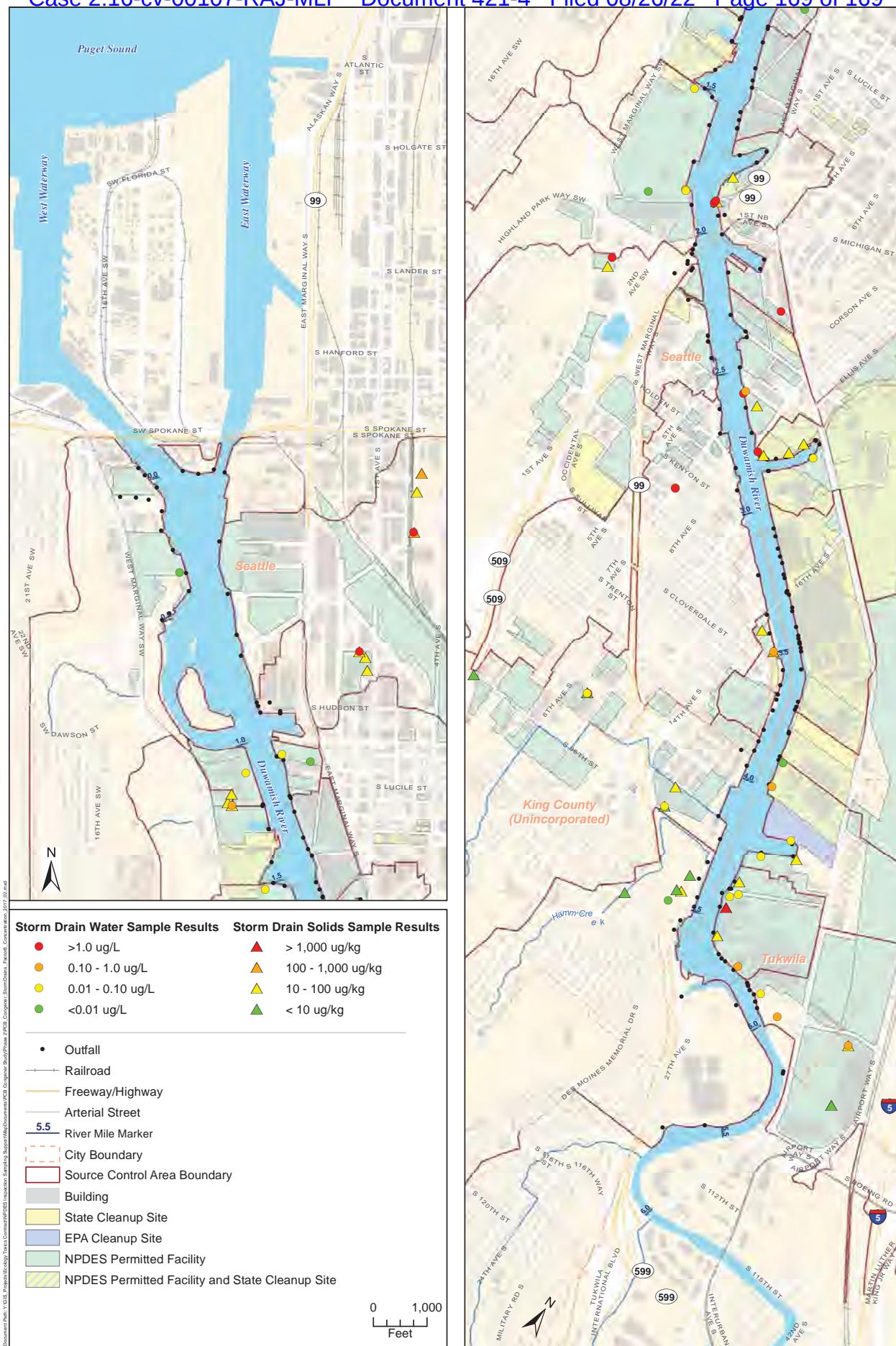


Figure 6. PCB Concentrations in Storm Drains, Factor 6 (PCB-209 and not similar to Aroclors)